An Investigation of Alternatives to Reductive Clearing in the Dyeing of Polyester

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ABSTRACT

Reduction clearing is commonly carried out as an after-treatment to remove deposits of disperse dye and other residual impurities from the surface of dyed polyester. The research described in this thesis establishes the positive effect of conventional reduction clearing using aqueous sodium dithionite under alkaline conditions on the colour and fastness properties of polyester dyed with a series of selected commercial disperse dyes at a range of depths of shade. Because of certain environmental, technological and economic disadvantages associated with traditional reduction clearing, there is industrial interest in alternative processes. This research also describes a study of some alternative approaches to clearing by means of the development of an understanding of the principles of clearing and its effect on the properties of polyester dyed with disperse dyes. The study involved the use of three organic reducing agents, formamidine sulphinic acid (thioureadioxide), hydroxyacetone and glucose, and also a previously-reported method using a simple detergent wash-off procedure. Besides the organic reducing agents, this study presents investigations concerning the use of enzymes and electrochemical methods in the reduction clearing of polyester. The relative merits of the alternative processes, in terms of the efficiency of surface dye removal, the effect on fastness and colour properties, the biochemical oxygen demand and chemical oxygen demand of the residual treatment liquors are discussed. The redox potential values of the reducing agents under application conditions have also been compared. The results throughout correlate closely with the efficiency of surface dye removal as assessed by acetone extraction of the dyed samples. Scanning electron microscopic investigations of dyed samples before and after reduction clearing are qualitatively consistent with the observations. The outcome of the clearing process varies with the particular dye used. Explanations have been suggested based on mechanisms proposed for the clearing processes in relation to specific characteristics of the molecular structures of the dyes.

DEDICATION

For mama je and papa je….

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Chapter 1 - Introduction

1.1 Background

Polyester (polyethyleneterephthalate, PET) fibres have emerged as having a leading share among natural and synthetic fibres when production and consumption of different fibres in the world is compared. It enjoys this dominant position due to its desirable properties, the most important of which are versatility and ease of use. It is also blended with natural fibres such as cotton and wool, mainly due to these characteristics, which are lacking in most natural fibres. Polyester and its blends find applications in a range of markets, such as apparel, upholstery and workwear as well as technical textiles, for example, non-wovens.

Polyester is dyed virtually exclusively with disperse dyes. Disperse dyes are non-ionic molecules of relatively small molecular size with limited solubility in water at room temperature. They are usually applied to polyester from a fine aqueous dispersion at relatively high temperatures where the solubility in water becomes sufficient to allow individual molecules in solution to come into contact with the fibres. Polyester fibres are relatively hydrophobic with a highly crystalline structure and are consequently difficult to dye at low temperatures. Dyeing is generally carried out at high temperatures, often around 130^{o}C, above a temperature referred to as the dyeing transition temperature, which is closely aligned with the glass transition temperature and where higher segmental mobility of the polymer chains enables the dye molecules to penetrate into the fibre. Because of the low solubility of disperse dyes in water and the tendency for particles in the dye dispersion to aggregate during the course of dyeing, some residual dye commonly remains on the fibre surface at the end of the dyeing phase. These surface deposits may have an adverse effect on the colour and fastness properties of the dyed fabrics, if present, and an aftertreatment to remove them is generally introduced into the dyeing process. The washing process which is used traditionally to remove the deposits of disperse dye from the surface of the polyester after dyeing is referred to as reduction clearing. This process involves treatment of the dyed polyester with an aqueous solution of a reducing agent in alkaline conditions at temperatures below the boiling point of water. Commonly, reduction clearing employs a solution of sodium dithionite, sodium hydroxide and a non-ionic surfactant at temperatures in the range 60–80°C for a period of 20–30 minutes [1-5]. Because of the hydrophobic character of polyester and since the process is conducted below the glass

transition temperature, the reducing agent and alkali, both ionic species, cannot penetrate into the interior of the polyester. Thus, only dye on the surface is removed while dye molecules that have diffused into the polymer during dyeing remain unaffected [6].

The most important disperse dyes used industrially belong to either the azo or the anthraquinone chemical classes. As the name implies, the clearing involves chemical degradation of surface dye molecules by reduction. It is commonly accepted that azo chromophores are reduced irreversibly to colourless primary aromatic amines, and removal of these small molecules is probably facilitated by the surfactant. Dyes based on the anthraquinone chromophore are reduced to their colourless or weakly coloured reduced (*leuco*) forms, which are soluble in aqueous alkali and may be removed in this form from the surface before re-oxidation can take place [7, 8]. In addition to the dye, there may be surface deposits of oligomers, mostly cyclic trimer derivatives of polyethyleneterephthalate, which are only sparingly soluble in water at the dyeing temperature and may crystallise as a white powder on the fabric and in dyeing machinery as the dyebath is cooled. These oligomers may also be removed by the clearing process [9].

Reduction clearing is of technical importance in polyester dyeing in order to improve the brightness of the colour and the fastness properties of the dyed fabric, especially to wet treatments [10]. There are, however, certain environmental, technological and economic disadvantages associated with the traditional reduction clearing process. The environmental disadvantage of the process is that it generates sulphur-containing degradation products derived from sodium dithionite which appear in the effluent with potentially toxic effects, notably sulphite (SO_3^{2-}), sulphate (SO_4^{2-}) and thiosulphate ($S_2O_3^{2-}$). Waste waters containing sulphites and sulphates are corrosive and can cause severe damage in waste lines [11, 12]. The oxidation products of sodium dithionite may also cause oxygen depletion in water streams resulting in an increase in chemical oxygen demand [4]. There are also issues associated with the formation of aromatic amines from the reduction of azo dyes. Another technical issue is the sensitivity of sodium dithionite to air oxidation in an alkaline medium at high temperatures, so that an excess is used to compensate for the loss. In addition, the aftertreatment requires pH adjustment from the acidic conditions during dyeing to the strongly alkaline clearing conditions for reduction clearing, followed by a final neutralization, and this increases the time and cost of the overall dyeing process. A number of alternative organic and

inorganic agents and some proprietary compounds have been proposed and marketed as replacements for sodium dithionite, but these do not appear as yet to have found significant commercial acceptance for a variety of reasons, associated mostly with environmental concerns, efficiency and cost [10, 11, 13]. In recent years, it appears that there is growing belief that the need for reduction clearing in the dyeing of polyester is diminishing as a result, for example, of the improved dispersion properties of commercial disperse dyes and the development of dyeing machinery with more efficient rinsing systems [14, 15]. Nevertheless, reduction clearing currently retains industrial importance especially for medium to heavy depths of shade, for package dyeing and the dyeing of loose fibres. In addition, it is important in the dyeing of polyester microfibers which require more dye than regular denier fibres to achieve equivalent depth [16], a feature that inevitably increases the level of dye deposition on the surface [3, 17].

1.2 Aims & Objectives

In spite of its commercial importance, there is remarkably little documented research aiming to quantify the outcome and the merits of reduction clearing in the dyeing of polyester. It is reassuring that this is an opinion shared by other authors [18]. Thus, one of the objectives of this research is to establish a more definitive understanding of the principles of the traditional reduction clearing process, such as the relationship between the effects of the treatment and specific features of the molecular structure of the dyes. This may be achieved by studying the effect of reduction clearing on the fastness and colour properties of polyester dyed with a range of disperse dyes of known chemical structures at different concentrations. Textile processing is a water-intensive sector and effluents of varying types and magnitude are discharged. Many industries have installed effluent treatment plants to meet the increasing stringent demands of environmental safety standards, but an approach to reduce the effluent and its hazards would have many advantages. The major objective of this study is to explore a range of alternative clearing agents and processes which offer the potential to minimise the environmental consequences associated with the use of sodium dithionite. The alternatives which have been studied in the research described in this thesis include organic reducing agents, enzymes and electrochemical methods. The three organic reducing agents that have been studied in this research are formamidine sulphinic acid (thioureadioxide), hydroxyacetone and glucose. All three of them act as reducing agent under alkaline conditions and have been used in dyeing applications previously. In contrast to the widespread investigation of the potential of these organic agents for the reduction of vat and sulphur dyes, there have been comparatively few studies of their

use as alternatives to sodium dithionite in the clearing of dyed polyester, and the reports which have appeared are limited in scope and detail. Thus, in this study, these organic reducing agents are investigated specifically for the reduction clearing of polyester. The reducing efficiency of the alternative clearing agents is to be related with their redox potential values.

Enzymes appear to be an attractive alternative due to their environment friendly nature and their growing use on textiles. Desizing of cotton by amylases is a well established practice. There are other instances of their use in textiles such as cellulases for bio-polishing of cellulosics, catalases for the removal of residual peroxide after bleaching and laccases for the bleaching of denim garments. The use of enzymes on polyester has yet to find wider commercial acceptance but research is underway on different levels. Lipases have been reported to increase the hydrophilicity of polyester by hydrolysing the ester groups of the polyester. This enzymatic treatment is able to improve the wetting characteristics of polyester at lower treatment temperatures and in shorter times than alkaline hydrolysis. The action of the enzymes is limited to the surface of the polymer due to its size and thus there is no loss of strength or mass, as is the case with alkaline hydrolysis. Polyesterases have also been used to increase the hydrophilicity of polyester by cleaving the ester group in the polyester chain resulting in the formation of carboxylic acid end groups. Cutinases have been used to hydrolyse the cyclic oligomers which may be present on polyester. Thus, to further the basic objective of exploration of alternatives for clearing of dyed polyester, this study aims to investigate two types of enzymes, one belonging to the hydrolase class and the other an oxidoreductase, as clearing agents for disperse dyed polyester. Indirect electrochemical methods involving the use of redox mediators have also been studied as potential alternative method for the reduction clearing of dyed polyester. This study also aims to assess the environmental impact of the selected alternative clearing agents and processes. For this purpose, chemical and biochemical oxygen demand values for the residual liquors of the alternative clearing processes are established as a means to assess the potential effect on the effluent.

1.3 Outline/Roadmap

The thesis is presented in classical style, comprising six chapters. This first chapter of the thesis provides an introduction to the research. It describes the background to the research, and its aims and objectives. A literature review of relevant topics is presented in Chapter 2. It includes a discussion of the nature of disperse dyes, dyeing methods for

polyester, a detailed description of the reduction mechanisms involving sodium dithionite and a discussion of the principles of alternative clearing agents used in this study. Chapter 3 provides an outline of the materials and methods employed for this research.

In the first section of Chapter 4, a preliminary study is reported in which an appropriate experimental methodology is established to allow evaluation of the principles and merits of traditional reduction clearing, as a necessary prelude to a more definitive exploration of alternative processes. The strategy for this section involves dyeing of polyester fabric with a series of selected disperse dyes at concentrations in the range 1-5% o.m.f which are then subjected to conventional reduction clearing. The dyed fabrics were evaluated in terms of the level of extractable surface dye, and the colour and technical performance, both before and after clearing. The enhancement in the fastness properties due to clearing was quantified and the influence on the colour of the dyed fabrics was assessed. In the second section, the study has been extended to reduction clearing with formamidine sulphinic acid (thioureadioxide), hydroxyacetone and glucose, using the same set of dyes and experimental assessment procedures. In addition, a comparison is made with the outcome of the detergent-based wash-off treatment which has previously been reported. Our study includes polyester fabrics dyed to the higher depths of shade that necessitate the use of clearing. In addition, some relationships between the effects of the treatments and specific features of the molecular structure of the dyes have been developed. The third section of chapter 4 involves the investigation concerning the use of enzymes as clearing agents for dyed polyester. The final section concerns a preliminary study of electrochemical methods as potential processes for reduction clearing. The efficiency of all the alternative processes is assessed by the level of surface dye as determined by the amount of extractable dye, effect on fastness and colour properties as well as scanning electron microscopy of the treated samples. The redox potentials of the clearing agents are also measured under the conditions used and the chemical and biochemical oxygen demand values for the residual liquors are established as a means to assess the potential effect on the effluent.
The most important overall conclusions from the research are presented in Chapter 5 while recommendations for the potential for future work are outlined in Chapter 6.

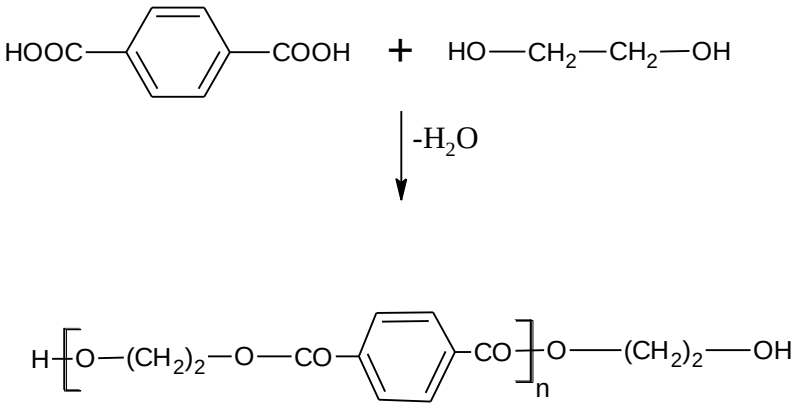
Chapter 2 - Literature Review

2.1 Polyester

Polyester is a generic name for polymers consisting of linear chains containing ester groups. Polyesters include polymers such as polyethylene terephthalate, polymethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate, polycarbonate, polylactide and polyethylene oxalate. The most common of the polyesters is polyethylene terephthalate (PET) and the term polyester used in this thesis refers to polyethylene terephthalate fibres. Though research on polyester had started in the 1920s, its commercial production began only in the 1940s, after the Second World War. Polyester was introduced in the commercial market later than other synthetic fibres, such as nylon and acrylic, which had a significant market share at the time, but by 1972, polyester had taken the place of nylon as the leading synthetic fibre [19]. Polyester took this dominant position due to its unique consumer properties as well as its use of cheap raw materials and manufacturing facilities. It has maintained its share in the world fibre market to this day and in this age, where every person in the world consumes about 8 kg of textile fibres in a year on average, polyester makes up about 3 kg of that quantity [20].

2.1.1 Structure

Polyester is a linear polymer manufactured by the esterification of a dibasic organic, commonly aromatic carboxylic acid with a dihydric alcohol, followed by condensation polymerisation as shown in Scheme 2.1.



Scheme 2.1 Formation of polyester

This direct esterification reaction is carried out under pressure at about 240°C using a slight excess of ethylene glycol in the presence of a small amount of a strong organic or inorganic base. The resulting product consists of linear oligomers with about 10

monomer units which are then polymerised by condensation at 280-290°C and 0.1 mbar to produce polymers of high molecular mass (at least 50 monomer units). At this stage, the polymer is in a molten state and can be fed directly to the spinning heads for extrusion or converted into chips which can be taken elsewhere for fibre production. Extrusion is the process where molten polymer is transformed into fibrous form by passing through spinneret heads. The spinneret is a perforated disc from where the polymers comes out as threadlines which are then attenuated by drawing and winding under fixed temperature and tension to achieve desired level of tensile properties. The fibres as it comes out from the spinning head and wound at speeds of less than 1500 m min^{-1} has a low degree of orientation. Most of the polyester yarns are manufactured using high winding speeds of 2500 - 4000 m min^{-1} resulting in a partly oriented yarn (POY) which is then drawn to a low draw ratio such as 1.5:1 [3].

Polyester, that is polyethylene terephthalate, can be modified chemically by replacing the monomers. For example, terephthalic acid can be replaced partially with dimethyl isophthalate and ethylene glycol can be wholly replaced with 1,3-propanediol. These modifications are carried out to introduce changes in the mechanical properties of regular polyethylene terephthalate [21]. Generally, polyester fibres are cylindrical with circular cross section but trilobal and hollow fibres are also prepared depending upon the end use [1]. Trilobal yarns are mostly used in carpets due to their ability to hide soil while hollow fibres provide very good thermal insulation and are thus utilized in bedding applications such as duvets. Specially constructed deep grooved polyester fibres which are commercially known as 4 DG fibres have several grooves on the cross section running parallel to the fibre axis. Such a cross section provides good capillary action and wicking properties [3]. The cross-sectional structures of polyester are shown in Figure 2.1.

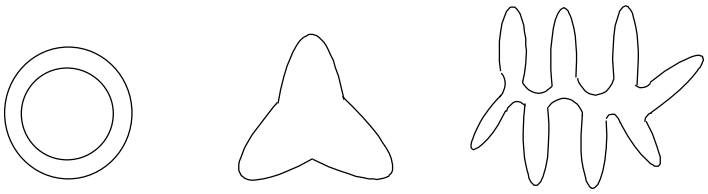


Figure 2.1 Cross-sectional structure of polyester fibre, (a) Hollow, (b) Trilobal, (c) 4 DG

2.1.2 Properties

Polyester has high tensile strength, high initial modulus and good resistance to weathering. It is a thermoplastic polymer and can be made dimensionally stable by heat treatment thus providing good resistance to creasing as well as good crease recovery. Polyester fibres absorb very little water and have a moisture regain of only 0.4% at 20°C and 65% relative humidity. There is no change in its properties arising from the absorption of water at ambient temperatures [1]. Due to its hydrophobicity, polyester resists common ionic chemicals in solution. At normal temperatures and pressures, the effect of such chemicals in aqueous solutions remains confined to the surface only [9]. It can be hydrolysed with a strong solution of alkali at elevated temperatures but this is a superficial effect only. Thus polyester is resistant to normal wet processing conditions and other agencies which a textile faces during its life. Another important property of polyester is its biological inertness which leads to its use in medical applications.

Glass Transition Temperature

The Glass transition temperature (T_G) of a polymer is the temperature at which the internal molecular structure changes from glassy state to rubbery state, that is, molecular segments start moving past each other. A polymer consists of amorphous and crystalline regions as shown in Figure 2.2.

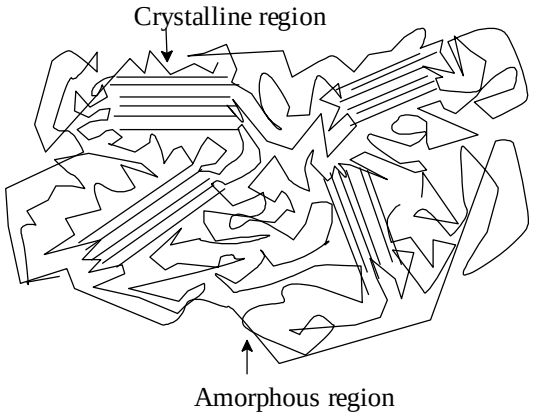


Figure 2.2 A schematic depiction of amorphous and crystalline regions of a polymer

In crystalline regions, the molecular chains are tightly and closely packed while in an amorphous region the chains are relatively irregular creating some free spaces in the structure. When heat is applied to thermoplastic polymers, it is absorbed by the molecular chains. At a certain temperature when the energy provided in the form of heat is sufficient to break the intermolecular bonds, the molecules start to slide past each other. Since there are no ionic or polar groups in polyester, the molecular chains are

held together through π-π interactions. As the intermolecular bonds are weakened, molecular chains can move around and change places creating voids in the internal structure. These changes are at a molecular level and take place slowly over a wide range of temperatures. All of these changes take place in the amorphous region only. As the mechanical properties of a polymer depend upon its structure, a concomitant change is observed in the polymer properties. Thus glass transition temperature is the temperature at which the behaviour of polymer changes from a glassy solid to a rubbery solid. It is a function of the supramolecular structure of the polymer and varies with the processing conditions such as draw ratio. Since these changes are quite slow, the glass transition, in fact, occurs over a narrow range of temperature instead of a sharp point. The changes in the physical properties are used to measure the glass transition temperature and the result can vary with the property studied. The glass transition temperature of a polymer depends upon its crystallinity; factors which increase the crystallinity result in a higher glass transition temperature. For example, polyester has a glass transition temperature of about 78°C in non-crystalline form; however, the glass transition temperature of a crystallised oriented fibre is about 120°C [3].

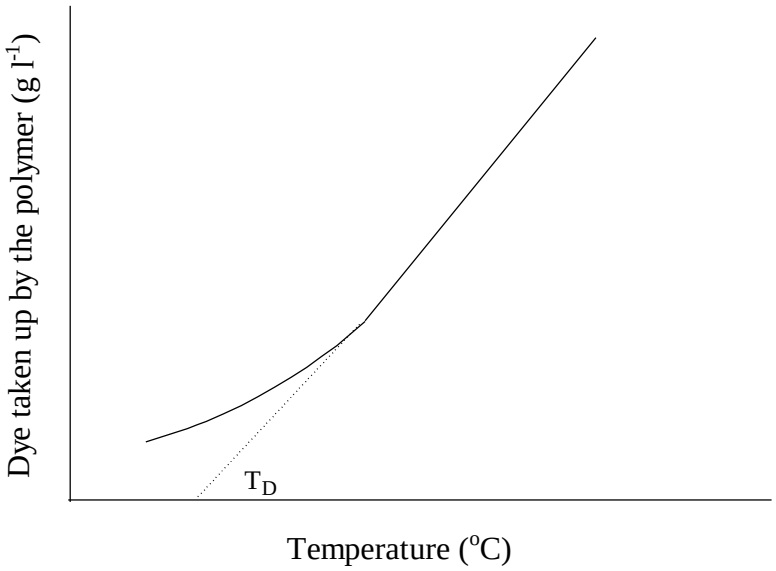


Figure 2.3 Plot of dye adsorbed by the polymer with temperature

Dyeing involves the diffusion of dye molecules in the polymer; below the glass transition temperature, dye molecules cannot diffuse into synthetic fibres, as there is not enough free volume inside the polymer for the dye molecules. The temperature at which a significant amount of dye molecules can diffuse into the polymer is referred to as the dyeing transition temperature. This temperature is obtained from a plot of dye

uptake versus temperature by extrapolating the dye uptake curve onto the temperature axis as shown in Figure 2.3 [22].

Mostly, the dyeing transition temperature (T_D) is slightly lower than the glass transition temperature (T_G). However in some cases, its value has been determined to be higher than the glass transition temperature. This observation leads to the conclusion that dyeing transition temperature also depends upon the interaction of the dye with the fibre [3]. At this temperature, the rate of dyeing of synthetic fibres increases significantly. The glass transition and dyeing transition temperatures are characteristics of synthetic fibres only and natural fibres do not exhibit these characteristics [2].

The properties of polyester which have been considered as its drawbacks are only a few. These properties include its lower water absorption and high glass transition temperature, which preclude its dyeing at lower temperatures. Another is its high mechanical strength due to which staple polyester fibres have a tendency to pill. These drawbacks have long been managed. For example, copolymerisation may be used to reduce the glass transition temperature and thus dyeing can be carried out at lower temperatures. However, other solutions to this issue are more widely employed, such as the use of a high temperature dyeing machine. Besides opening up the fibre's polymer structure, high temperature also influences the dyeing medium and dye molecules. A rise in temperature results in a consequent increase in the kinetic energy of the dye molecules and reduces the viscosity of water. Thus, high temperature improves the rate of dyeing by influencing all the three major components of a dyeing process. Heat setting of polyester may reduce its tendency towards pilling or alternatively copolymerisation to produce lower tenacity polyester fibres can be helpful in this respect [1]. Due to its high hydrophobicity, polyester has a tendency to build up static charges. This can be overcome by copolymerisation or by applying antistatic finishes [3]. To summarise, the advantages of polyester outweigh its shortcomings.

2.1.3 Oligomers

As with all polymers manufactured by condensation polymerisation, polyethylene terephthalate polymers have a certain proportion of low molecular weight compounds which are referred to as oligomers. The largest proportion of these oligomers is found in melt spun polymers where they are found in equilibrium with polyethylene terephthalate. Their quantity varies from 1.5% to 3.5% and they include cyclic trimer,

pentamer and a dimer. The most important of these oligomers with regard to dyeing is the cyclic trimer of polyethylene terephthalate as illustrated in Figure 2.4.

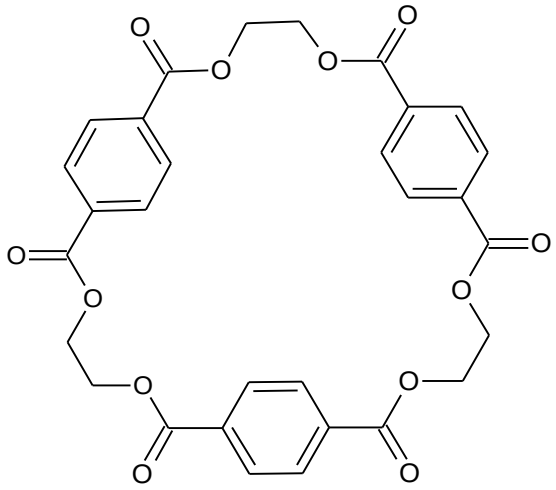


Figure 2.4 Cyclic trimer of polyethyleneterephthalate

Oligomeric material can be extracted from the polymer with some solvents, such as dioxan and the degree of removal varies with the solvent. However, when the polymer is re-melted after extraction of the oligomers, the cyclic trimer is formed again [3]. It has a very low aqueous solubility, 0.4 mg l^{-1} at 100°C and a high melting point of about 315°C. It diffuses out of the polymer onto the surface under high temperatures, for example at 130°C, more so in the presence of water than dry heat and during steam heat setting. The oligomer molecule is about three times the size of that of a typical anthraquinone disperse dye and thus, migrates more slowly than the dye. At temperatures above the glass transition temperature of polyethylene terephthalate, such as those that are used during high temperature dyeing, oligomers migrate out of the fibre on to the surface. The extent of migration increases with an increase in treatment time. The oligomers have a tendency to deposit on the surface of the polyester and on the dyeing machine on cooling. These surface deposits are not dyed by disperse dyes and remain firmly attached to the fibre while they appear as a white dusting powder on the machine parts. They also provide centres for nucleation of disperse dyes under favourable conditions thus destabilising the dispersion and forming dye spots on the fabric. The presence of oligomers also produces a delustering effect on the shade of a dyed fabric. During package dyeing, oligomer deposits may act as a filter and reduce the liquor flow through the packages. These surface deposits also affect the frictional characteristics of polyester yarns during melt spinning [9, 15]. The oligomers cannot be removed permanently and so the processes have to be designed accordingly. Surface deposits of oligomers are reduced after treatment at temperatures in the range used for

thermofixation, which is at 210 – 220°C. These deposits can be reduced by discharging the dyebath at high temperature after dyeing. However, this requires special arrangements for discharging the bath under high pressure. In the case of jet dyeing, there is a possibility of rope marks appearing on the polyester fibre fabric since it is above the glass transition temperature [2]. Presumably, most efficient method for the removal of oligomers is reduction clearing.

2.1.4 Microfibres

Generally fibres with a count less than 1 decitex are said to be microfibres. A conventional polyester fibre has a count of 2 -5 dtexpf whereas a polyester microfibre is not more than 1 dtexpf and most commonly around 0.5 dtexpf. Such fine filaments when used in fabrics exhibit excellent textile properties such as softness, flexibility and drape. A reduction in the linear density of the fibre results in an increase in the surface area of the resulting yarn. For a given count, microfibres have at least four times the surface area of a regular fibre. The decrease in linear density is accompanied by a corresponding reduction in the strength of the filament. However, the strength of the yarn is not affected because more filaments are present in a given count as shown in Figure 2.5.

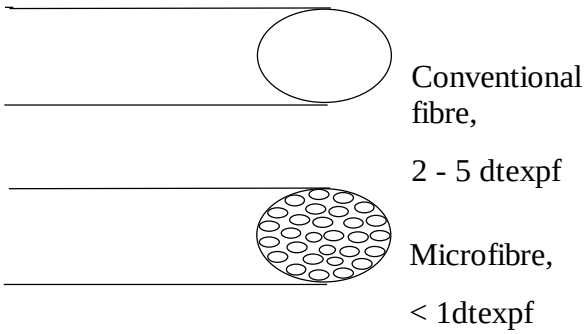


Figure 2.5 Schematic representation of conventional and microfibre polyester filaments

Microfibre fabrics have a high density per unit area which makes them windproof and waterproof. However, water vapour can pass through thus making them comfortable to wear. Such fabrics are used advantageously in sportswear, active wear and outer wear [23]. Microfibre fabrics also have radiant heat–insulating properties. The diameter of the filaments in a microfibre of 0.5 dtexpf is about 7µm which is of the same order as the wavelength of infrared radiation (2 – 20 µm). Thus the infrared radiation is scattered from the microfibre fabric and in a garment constructed from polyester the heat of the body is retained. One disadvantage of the microfibres is their low thermal capacity, due to which they can be easily overheated. This can create trouble during

ironing. Such fabrics are also prone to snagging and need to be handled with care [3]. The implications of these physical differences on the dyeing and fastness properties of the microfibre fabric are significant and are discussed in Section 2.3.2.

2.1.5 Applications

Polyester fibres find applications in almost every sphere of our life. Polyester is widely used in apparel fabrics such as shirts and trousers because of its good wearing properties and easy maintenance, which is generally referred to as "wash and wear" property. They can be used as pure polyester and in blends with cotton or wool in such applications. Polyester (4 DG) is used in sportswear as it wicks the moisture away from the body due to its grooved cross-section (Figure 2.1) and is quick drying. It is also used in household furnishings and upholstery, as fabric and fibre-fills. Its high strength and good resistance to physical and chemical changes makes it an ideal material to be used in automotive fabrics and industrial uses such as tyre cords, filter fabrics, sail cloth etc. It is used in medical textiles, such as surgical sutures because of its biological inertness and biodegradability. The latter property is not found in the traditional polyester but is only a characteristic of some specifically developed biodegradable polyesters such as polylactides [24].

2.2 Disperse Dyes

Disperse dyes are defined as substantially water insoluble dyes which have substantivity for one or more hydrophobic fibres, such as cellulose acetate, polyester and are applied from a fine aqueous dispersion in which some of the dye is in solution form [6, 25]. They were first developed for the dyeing of cellulose acetate but were later modified for the dyeing of polyester. One of the differences between dyes for acetate and for polyester is that the polyester dyes generally have a higher relative molecular mass. Disperse dyes for polyester are generally required to have a high ratio of mass to polarity. The balance between the hydrophobicity and hydrophilicity of a disperse dye is maintained to achieve a stable dispersion and good dyeing properties [26]. Dyes for polyester also have improved dispersion properties which are achieved by grinding the dye to a finer particle size and by using dispersing agents. Dispersing agents facilitate the milling to produce fine particles and help stabilise the dispersion during dyeing. The other major difference between the dyes for cellulose acetate and polyester is in the sublimation fastness. The earliest disperse azo dyes had poor fastness to sublimation which was improved by increasing the molecular size of the dye or by incorporating polar groups in the dye molecule [27].

Disperse dyes are low molecular weight compounds with relative molecular mass (ratio of the mass of a molecule to the unified atomic mass unit) of 300 – 600, having no charged groups but carrying some polar substituents which impart a small but important solubility to the dye. Disperse dyes are manufactured in the form of small particles, less than 1 μm in size. The aqueous solubility of disperse dyes exhibit a wide range of values and at 80°C varies from 0.2 to 100 mg l^{-1}. Since the solubility increases with an increase in temperature, at 130°C it increases to about 1 – 1000 mg l^{-1} and practically all of the disperse dye is in solution form [9, 28]. Conversely on cooling, the dye may precipitate out of the solution causing the dispersion to become unstable [5].

An important characteristic of disperse dyes is that they melt and vaporize when heated. Vapour pressure is inversely related to the molecular mass and polarity of the dye [26]. The vapours of disperse dye are absorbed by polyester because of the inherent affinity of the dye molecules for the fibre. Generally, the affinity of the dye for a fibre is influenced by its polarity, molecular mass and geometric shape. This unique property of disperse dyes, that is, vaporisation and absorption in vapour phase is utilised in thermofixation dyeing and transfer printing.

Though most of the disperse dyes are blue, red, orange, yellow, violet and brown, green and black dyeings can be obtained. However, green and black disperse dyes are difficult to synthesize as individual dye molecules due to a number of limiting factors. These are that the structure should be non-ionic and small with sufficient substantivity for hydrophobic fibres as well as ease of diffusion into the polymer. Black disperse dyestuffs are available in market which are a mixture of navy, red and yellow or orange dyes [6].

2.2.1 Types of Disperse Dyes with respect to Chromophore

Disperse dyes can be grouped into three major types, azo, anthraquinone and nitrodiphenylamine, depending upon the type of chromophoric structure [29].

Azo disperse dyes cover the whole spectrum. They are mainly yellow, orange and red dyes. There are a few blue and violets also. It is the largest and most important class consisting mainly of aminoazobenzene derivatives which are of the donor-acceptor chromogen type and can be represented as shown in Figure 2.6.

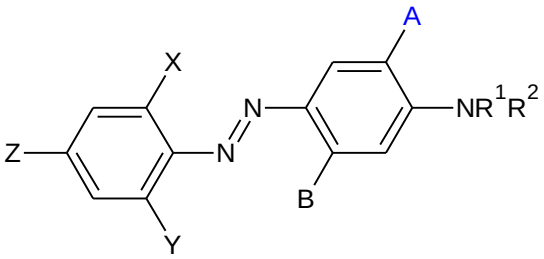
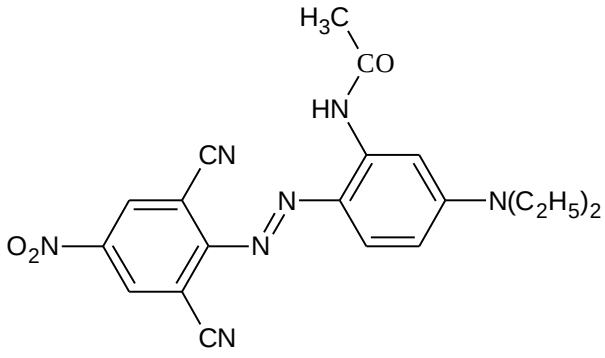
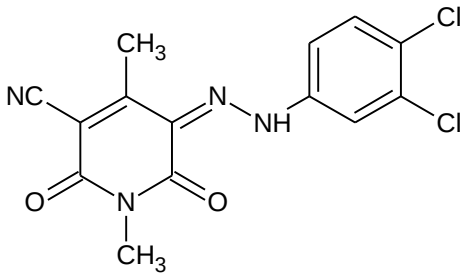


Figure 2.6 General structure of dyes based on aminoazobenzene

Generally, the substituents X, Y and Z are electron withdrawing, whereas A and B are electron donating. Variations in R^1 and R^2 are associated with changes in substantivity, light and wetfastness as well as hue. Electron releasing substituents on the coupling component produce a bathochromic effect (red shift) while electron attracting substituents produce a hypsochromic effect (blue shift). The ability of the substituent groups of the dye to form hydrogen bonds with the polymer affects the sublimation fastness. A free hydroxyl group in the side chain increases the basicity of amino groups, leading to better thermofixation fastness but poor light fastness. Cyano and acetoxy groups are electron deficient, and reduce the basicity of the tertiary amino group of the coupling component used in the synthesis of azo disperse dyes. Thus, acylation of the hydroxyl group improves the lightfastness but lowers the sublimation fastness. Hence, modification of the dye structure may affect one property at the expense of other and the inter-relationships are often complex [27]. Some examples of azo disperse dyes are shown in Figure 2.7.



(a) CI Disperse Blue 165



(b) CI Disperse Yellow 241

Figure 2.7 Examples of (a) azo and (b) hydrazo disperse dyes

Azo dyes generally exist in a *trans* configuration. Partial isomerisation to the *cis* form can occur on exposure to light. This change can produce a temporary colour change which is referred to as photochromism. The lifetime of the *cis* isomer is generally short in dyes with powerful electron donor groups and the original colour is restored after

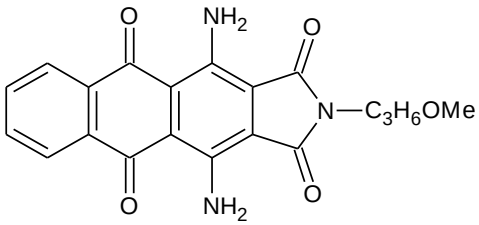
sometime. Thus photochromism rarely becomes a problem in aminoazobenzene dyes [30].

Azo disperse dyes are convenient and inexpensive to manufacture, while exhibiting generally very good fastness properties. However, they sometimes lack the brightness and lightfastness of anthraquinone and heterocyclic disperse dyes [27]. This shortcoming has been resolved by synthesizing azo dyes consisting of heterocyclic structures in the coupling or diazonium component. Such heterocyclic azo dyes have good brightness and high tinctorial strength [31]. Another problem that arises with azo dyes is their tendency to undergo reduction under high temperature dyeing conditions, that is, at 130°C [32].

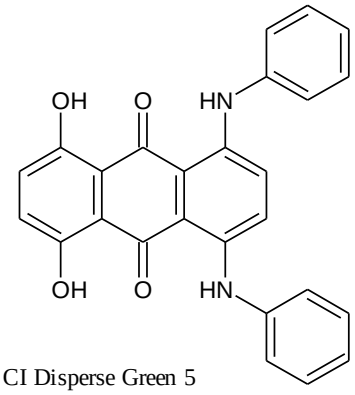
Azo dyes containing a hydroxyl group conjugated to the azo bond exhibit tautomerism. Such dyes exist as an equilibrium mixture of two tautomeric forms, azo and hydrazone, in aqueous solution. When the hydroxyl group in the question is at an ortho position to the azo bond, as shown in Figure 2.7(b) for CI Disperse Yellow 241, the hydrazone form is preferred. However, when the dye does not have a hydroxyl group (Figure 2.7(a), CI Disperse Blue 165) or if the hydroxyl group is phenolic, the azo form predominates [33].

With the increasing focus on environmental health and safety, azo dyes have come under strict scrutiny regarding their influence on health and safety. Thus according to German regulations, an azo dye that can form a carcinogenic aromatic amine on reductive cleavage is considered a carcinogen itself. Fortunately, the majority of the azo dyes in current commercial use do not produce carcinogenic aromatic amines [34].
Anthraquinone dyes constitute an important and large class of disperse dyes. A few examples of anthraquinone disperse dyes are shown in Figure 2.8. They normally give bright colours such as bluish reds, violets, blues and bluish greens. Their advantage is stability under most application conditions unlike azo and styryl dyes which undergo hydrolysis or reduction during high temperature dyeing. On the downside they are relatively expensive [27, 31]. As discussed in the previous paragraph, it is difficult to obtain the required level of sublimation and good lightfastness properties with azo disperse dyes. Anthraquinone dyes do not cause such a problem and are thus, commonly used for transfer printing. They also provide good coverage and level dyeing properties. Their excellent lightfastness properties make them particularly suitable for automotive applications. They can be used to dye blends of polyester with

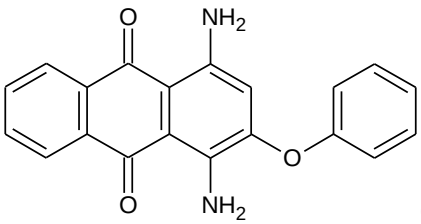
other synthetic fibres, such as nylon. However, in medium to heavy depths of shade, they are prone to stain nylon in an adjacent multifibre fabric if heat set before the washfastness test. In this respect, monoazo disperse dyes generally perform better than anthraquinone dyes and do not stain nylon [35].



CI Disperse Blue 60



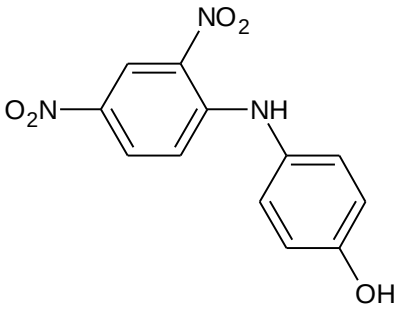
CI Disperse Green 5



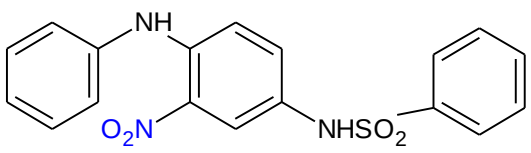
CI Disperse Red 60

Figure 2.8 Examples of anthraquinone disperse dyes

Nitrodiphenylamine dyes as shown in Figure 2.9 are a small group of mainly yellows and orange-yellows. Like azo dyes, they are economical and easy to manufacture. They give good lightfastness properties but have low tinctorial strength and build-up properties [36]. These dyes were originally developed for cellulose acetate and give poor sublimation fastness on polyester. However, sublimation fastness of such dyes can be improved by the introduction of polar groups or by increasing the molecular size [36]



CI Disperse Yellow 1



CI Disperse Yellow 42

Figure 2.9 Examples of nitrodiphenylamine dyes

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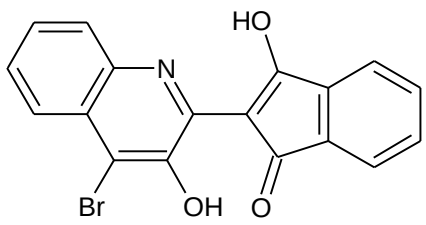
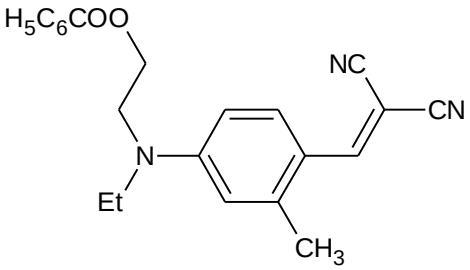


CI Disperse Yellow 64



CI Disperse Yellow 90

Figure 2.10 Examples of disperse dyes having miscellaneous chromophores

There are some other miscellaneous chromophoric structures utilised in disperse dyes. These include styryl chromophore such as in CI Disperse Yellow 90 and dyes based on heterocyclic ring systems, for example CI Disperse Yellow 64, as shown in Figure 2.10.

2.2.2 Types of Disperse Dye with respect to Dyeing Properties

Rate of dyeing, levelling properties, heat and sublimation fastness are influenced by the size and polarity of the dye molecule whereas lightfastness does not depend inherently upon the size. Hence, disperse dyes were originally classified by ICI, in the UK, in four groups, A, B, C and D, with respect to their sublimation fastness and dyeing behaviour. A graphical representation of the four classes of disperse dyes is depicted in Figure 2.11. It can be observed from the diagram that the dyeing properties of the disperse dyes tend to improve as the sublimation fastness decreases. Class A dyes have best dyeing properties in that they may be applied under mild conditions but lack sublimation fastness while Class D dyes have highest fastness to heat but poor dyeing properties [7]. Class A dyes have limited use on polyester and were originally developed for cellulose acetate. They can be used for the dyeing of polyester for certain uses but they may contaminate the machine during heat fixation because of their poor sublimation fastness. Thus they are not suitable for thermofixation dyeing [37]. Class B dyes show excellent dyeing behaviour on polyester. They have moderate sublimation fastness and give good coverage of physical variations in the fibre. Hence, class B dyes are used for the dyeing of texturised polyester. Class C dyes have better sublimation fastness than class B dyes. Dyes with good sublimation fastness properties are suitable for high temperature as well as carrier dyeing. They can also be used for thermofixation within the temperatures 190 – 210°C and their fixation is almost constant in this range. Thus any variation in temperature within this range will not lead to unlevel dyeing.

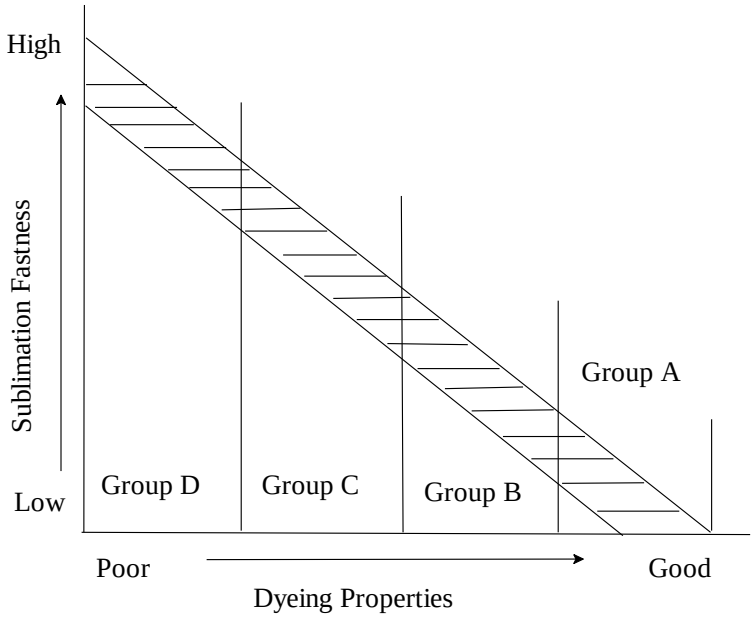


Figure 2.11 Relationship between dyeing properties and sublimation fastness of disperse dyes

As shown in Figure 2.11, class D dyes give best sublimation fastness properties. These dyes were developed for dyeing polyester slubbing, loose stock and yarn in high temperature dyeing machines at 130°C. They are suitable for thermofixation but not suitable for carrier dyeing. However, they require high temperatures for thermofixation [37].

In the USA, disperse dyes are classified into three classes as low, medium and high energy types. They cover the same range of properties as the ABCD classification. For example, low energy dyes belong to group A, medium energy dyes correspond to groups B and C while high energy dyes can be referred to as group D dyes [6]. The ABCD classification has now become obsolete and today disperse dyes are widely classified by the manufacturers according to their energy type.

2.2.3 Behaviour of a Disperse Dye in a Dispersion

When a particle is suspended in a medium, there are a number of forces acting on it which depend upon the nature of the particle as well as that of the medium. It is well known that the different states of matter are the result of varying strengths of the intermolecular attractions. In the case of solids, the intermolecular forces are quite strong, giving them a particular form and maintaining that shape. The intermolecular forces in a liquid are strong enough to restrain it to a particular volume without giving any shape and the liquids thus adopt the shape of the vessel in which they are contained.

The intermolecular forces present in a gas are the weakest of the three states of matter. As a result, gases do not have any shape and occupy all the space available to them. Solids and liquids have a surface which acts as a boundary layer between them and their surroundings, keeping them confined in a specific space. Gases, however, are devoid of any such surface. The surfaces of solids and liquids thus exist due to the presence of strong intermolecular forces. A more appropriate term for a surface is interface. Due to the presence of a distinctive phase boundary, the molecules of solids and liquids present at the interface behave differently than the molecules in the bulk. The molecules in the bulk are surrounded by similar molecules in all directions, so that the forces on any single molecule in the bulk cancel. On the other hand, the molecules present at the interface are subject to forces in two opposite directions, firstly attractive forces towards the interior of the solid or liquid and secondly the force from the outer phase. This second force can be attractive or repulsive depending upon the nature of the medium and the particle. As a result of the different kinds of forces acting on them, the surface molecules acquire a certain amount of energy which is proportional to the net magnitude of the forces acting on them. This energy is equivalent to the work needed to separate the surface molecules and is called interfacial energy. As the name suggests, this is a property of surface or interface molecules only [38]. If the attractive forces from the outer medium are stronger, the molecules at the interface would tend to move towards the outer medium. This would eventually result in the dissolution or miscibility of the two phases. In the case of disperse dye particles (which are essentially hydrophobic) in an aqueous medium, the outer medium exerts repulsive forces on the interfacial molecules, pushing them towards the centre of the particle. Thus disperse dyes cannot be dissolved in water, at least at low temperatures; instead, they form a colloidal dispersion [39, 40].

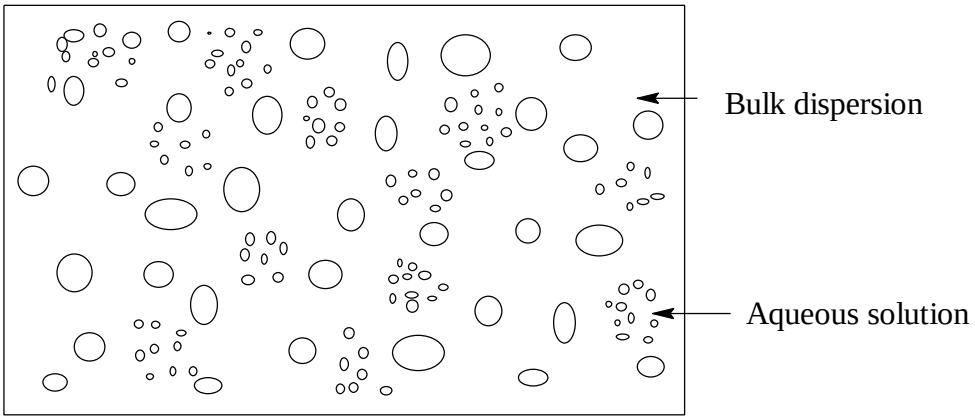


Figure 2.12 Schematic of the state of disperse dye in dispersion

A colloidal dispersion consists of dispersed particles in a continuous phase and is an intermediate state between solution and suspension. It is composed of two phases, the dispersed phase and the dispersion medium, corresponding to the solute and solvent in the case of a solution respectively. A phase is that part of a system which is chemically and physically homogeneous in itself. As disperse dyes do not have ionic groups and the particle size is greater than 1 nm, they do not form a solution in water. However, the size of disperse dye particles is less than 1000 nm which is smaller than the size of particles in a suspension and the presence of polar groups makes them slightly soluble in water so that the system is not classified as a suspension either. Thus, it can be said that the state of the disperse dye in water is a dispersion interspersed with some small regions of dye solution as shown in Figure 2.12.

According to the concept explained above, the attractive forces between the different molecules of disperse dyes predominate resulting in the formation of aggregates. Thus a disperse dye in water can be thought of as being surrounded by a hostile environment and other disperse dye molecules may be regarded as friendly; by attaching with these friendly entities, disperse dye molecules can create a safe haven for themselves where they are protected from the outside hostile environment. This happens when the molecules randomly collide with each under the influence of Brownian movement as the molecules should be close enough for the London dispersion forces to be effective. A solution is obtained only when the solute and solvent have a similar nature. However, in the case of a disperse dye, which is quite dissimilar to water, a solution is not possible because if the molecules of disperse dye leave the surface they face a hostile environment in the bulk where they have to do more work to remain suspended. The lowest energy state is only possible when they remain closely attached to molecules of a similar nature thus giving rise to the aggregates of disperse dye.

To obtain a solution of the disperse dye some other arrangements have to be sought. The first thing is to ensure that the size of the particles is small. There is a limit to the smallest particles size which can be obtained for disperse dyes. However, there has been significant progress since the first disperse dyes were synthesised, and the size of disperse dye particles has been reduced from 2 - 4 μm to currently less than 1 μm. This has still not reached the domain of the size of the particles in a solution. As the size of the particles decreases below 1 μm, the total surface area of the particle increases. This means that there is a larger number of molecules at the surface of a small particle than a large particle resulting in a higher interfacial energy and instability of the smaller

particles. For a macroscopic system, the interfacial energy of a phase and the number of molecules at the interface is negligible compared to its chemical potential and the number of molecules in the bulk. However, in colloidal systems, the number of interfacial molecules is not negligible when compared with the number of bulk molecules. This characteristic confers special properties on the colloids, one of which is colloidal solubility.

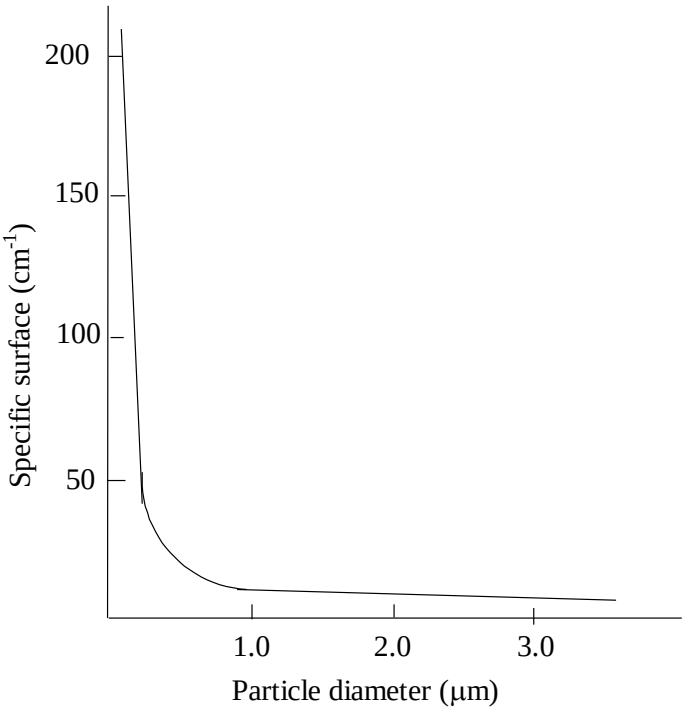


Figure 2.13 Relation between surface area and size of a spherical particle

Solubility is the capacity of a medium to contain another compound such that the result is a homogeneous medium. The term solubility indicates that the solute and solvent are in a state of equilibrium under a particular set of conditions. Colloidal solubility and macroscopic solubilities are different. Macroscopic solubility can be used in those cases where the solubility is independent of the particle size. Below a diameter of 1 μm, the specific surface increases very rapidly as shown in Figure 2.13. These small particles have an increased intrinsic energy which makes them unstable. When dispersed in a solution, such particles tend to move towards a lower energy state which is towards the solution phase or towards coarser particles to reach a state of equilibrium. A colloidal system is polydisperse in nature and is thus unstable. As the smaller particles disappear resulting in the formation of coarser particles, the solubility equilibrium also changes. The new equilibrium will be based on the coarser particles with lower solubility. Thus true solubility equilibrium cannot be reached in colloidal

systems and a solubility determined under a particular set of conditions will decrease with time. A disperse dye dispersion is inherently unstable and if it reaches equilibrium it ceases to be a dispersion. The solubility values of disperse dyes which are quoted in the literature are for macroscopic solubility only and should be considered with care before making any generalisations. Thus for a colloidal system the dissolution properties are more important than the solubility. Both solubility and rate of dissolution are higher in colloidal systems. Other important factors which influence the solubility of colloidal systems are:

- Particle diameter - small particles have higher solubility than large particles of the same compound.
- Ostwald ripening - this is the increase in size of the larger crystals of a compound, especially a sparingly soluble compound, as the smaller and more readily soluble crystals disappear [41]. The driving force for the Ostwald ripening is the difference in the solubilities of the particles in a polydisperse system. This creates a concentration gradient between smaller and larger size crystals and the compound transfers through the solution from higher energy to lower energy particles. This ageing process depends upon the size distribution, rate of dissolving, rate of crystal growth and the transfer through the solution. These in turn are influenced by time and temperature. However, it should be realised that the particles of the disperse dye are not spherical and thus Ostwald formula is not strictly valid.
- Change in crystal modification - if the crystal shape differs much from the equilibrium shape, the rate of crystal growth increases. This happens when the disperse dyes are ground to provide a fine particle size and as a result the crystal structure is deformed. As the particles are mechanically ground, the internal stresses increase making the smaller particles highly unstable resulting in an increase in solubility as well as the Ostwald effect. The energy content of the particles is influenced by both the size and state of surface molecules.
- Activation of particles by mechanical stress during grinding - on grinding, the crystal particles undergo deformations resulting in thermodynamic and structural instability and in such a state the reverse process, that is the recrystallisation, becomes spontaneous. As the energy content of the particles increases, their solubility in water and fibre increases also.
- Change of crystal habit in the presence of surface active agents [42].

The above discussion makes it clear why the disperse dye dispersion is prone to destabilisation. While all of the above mentioned factors are related to causes that are beyond the control of a dyer and can only be managed during the synthesis of the commercial dye preparation, there are other factors which are under the control of the dyer. These include dye concentration, temperature, time, pH, electrolytes, auxiliaries, materials present on the fibre and stirring. Dye particle agglomeration increases with an increase in dye concentration, temperature and dyeing time. Sudden temperature changes can also induce crystallisation. However, dispersion stability does not depend upon pH within the range 4 -6. Metallic ions such as calcium, magnesium and copper are undesirable. Vigorous stirring can also have an adverse effect on the dispersion stability [43].

2.2.4 Dispersing Agents

The other means that may be used to increase the solubility of disperse dyes besides decreasing the particle size is the addition of dispersing agents. Dispersing agents have two major functions for disperse dyes. Firstly, during the manufacture of disperse dyes, dispersing agents help break down the aggregates during milling of the dyes. Secondly, dispersing agents help to disperse the dye while preparing the dye dispersion for dyeing and stabilise it under the application conditions. From 20 – 60% of commercial disperse dye preparation consists of dispersing agents.

As discussed in the previous section, the term dispersion means a system of several phases in which one substance is finely divided in another, which is the dispersion medium. A dispersion may contain primary particles, agglomerates and aggregates. Agglomerates are clusters of particles that are held by relatively weak forces and are thus easily redispersible. Aggregates are masses of particles that have amalgamated. Thermodynamically, dispersions are in a metastable state. They have a tendency towards an increase in particle size which leads to a decrease in the free energy of the system. Increase in particle size is due to processes referred to as agglomeration, coagulation, flocculation or coalescence. These may lead to the destabilisation of dispersion. Dispersion of an insoluble powder in water or any other medium takes place in the following stages.

1. Wetting of the powder by the liquid.
2. Breaking up the clusters into smaller particles.
3. Stabilisation of the dispersion.

The most important stage is to maintain the dispersed particles in the dispersion and prevent the formation of agglomerates. Wetting denotes the action of bringing the solid phase in contact with the liquid phase and to replace the solid-air interface with a solid-liquid interface. Surfactants promote the wetting process by decreasing the interfacial tension and contact angle. On wetting the powders, the liquid penetrates the agglomerates displacing the air trapped between them, resulting in the disintegration of the agglomerates. However, the breakdown of aggregates and primary crystal particles needs mechanical energy in addition to the surfactant. It has been suggested that microcracks develop in the crystal particles on the application of mechanical energy but the cracks are joined again on the removal of pressure. In the presence of surfactants, these cracks are filled by the surfactant molecules, thus, preventing the reformation of crystal particles and enhancing the disintegration. Thus, less mechanical energy is required in the presence of surfactants. When the ionic surfactants adsorb on the particles, the particles acquire an ionic charge. Similar electrical charges cause repellent forces which become greater than the adhesion forces. This in turn leads to spontaneous dispersion. A stable dispersion indicates that the total number of suspended particles remains unchanged. The first step in the stabilisation of the dispersion by a surfactant is the adsorption of the surfactant from the solution on the interface of solid particles. Surfactants are adsorbed in a state vertically oriented to the nonpolar interfaces of the dye particles. In both ionic and non-ionic surfactants, the hydrophobic part of the surfactant molecules faces towards the solid dye particles while the hydrophilic part points towards the aqueous phase. The adsorbed ionic surfactant molecules form an electrical barrier which prevents the aggregation. Polyelectrolyte dispersing agents which have many ionic groups in their molecules, are effective in this regard. However, as the number of hydrophilic groups in the surfactant molecule increases, its adsorption decreases, thus reducing the stabilising effect of such dispersing agents. Many dispersing agents have a maximum dispersing effect which depends upon the substrate, and the relationship between hydrophobic and ionic groups [41].

Dispersing agents can be either surfactants or polymers. Surfactants are small molecular weight amphiphilic compounds, that is, they have both hydrophobic and hydrophilic components in their molecule. Their structure commonly has an ionic head and a hydrocarbon tail. Surfactants can be also be classified according to the type of the charge of the functional head, they may be cationic, anionic, nonionic and amphoteric. For disperse dye dispersion, anionic or non ionic dispersing agents are used [41].

Dispersing agents used with disperse dyes are mostly ligninsulphonates and condensates of naphthalene sulphonates with formaldehyde. These dispersing agents contain readily polarisable, aromatic hydrophobic groups and several ionic groups [41]. The degree of sulphonation of the lignin sulphonates and the molecular mass of the unsulphonated materials from which they are derived have a major influence on the milling and stability of dye dispersion during dyeing. A high degree of sulphonation is advantageous during the milling process but it decreases the dispersion stability at high temperatures. Disperse dyes with a high degree of hydrophobicity are less sensitive to high temperatures, and thus sulphonated dispersing agents can be used in this case. This is because such products are easily adsorbed on the hydrophobic dye particles and cannot be removed easily by thermal agitation. On the other hand unsulphonated or low sulphonated dispersing agents can be used with disperse dyes with more polar groups [44]. The shape and size of the disperse dye particles are influenced by the type of the dispersing agent used during the coupling reaction for azo dye synthesis. For example, in the case of CI Disperse Yellow 3, non-ionic surfactants, such as secondary alkyl sulphates and sodium laurylsulphate, promote the formation of well crystallised particles. Quaternary ammonium surfactants were observed to induce a gel type precipitate while the use of non-ionic surfactants result in the formation of well rounded particles which are easier to mill [45]. The problem with lignin sulphonates is that they have a tendency to reduce azo dyes under high temperature dyeing conditions and cause staining of the fibres, which in the case of polyamides and wool may result in yellowing of the fibre on exposure to light. They have a tendency to foam as well, which can create processing issues [41].

Nonionic surfactants of the polyethylene oxide type stabilise by a steric hindrance mechanism. The hydrated coils of polyethylene oxide chains project towards the aqueous phase opposing mutual attraction of the dye particles [44]. Dispersing agents based on polymers often form a gel, restricting the movement of particles. Thus, even a suspension of coarse particles can be converted into a stable dispersion by using these polymer dispersing agents [41].

High quantity of dispersing agents can decrease the dye diffusion into the polymer thus lowering the dye yield in thermofixation. This issue is more pronounced for 100% polyester than in polyester blends with cotton. Liquid dye formulations have a lower quantity of dispersing agents and this can be helpful in improving the dye yield. During drying of polyester cotton blends before thermofixation, dye migration results in

problems such as face to back variation, side to side variation, blotchiness and streaks. Anionic polyelectrolytes are used as migration inhibitors in such cases. They also improve the dye yield by preventing dye aggregation. The organic polymer forms a film coating on the dye particles during drying which does not melt at the thermofixation temperature but can be redissolved easily in alkaline or neutral water. At lower concentrations, the film does not interfere with the vaporisation of disperse dye and its subsequent diffusion into polyester. However, a thick film may have the opposite effect [45].

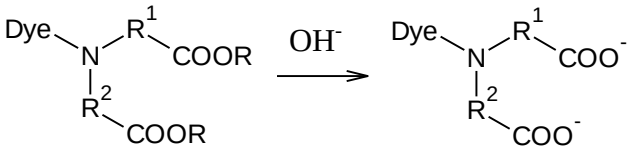
Nonionic surface active agents possess water solubility due to the polyether chains. Their water solubility decreases with an increase of temperature. At a certain critical temperature, which is characteristic of each agent, they become insoluble in water and can form an emulsion or a sticky precipitate. This critical temperature is referred to as the cloud point [1]. If the cloud temperature of nonionic surfactants is lower than the dyeing temperature, they may form a sticky precipitate with the dye resulting in staining on the fabric. The cloud point of nonionic surfactants is increased by increasing its degree of ethoxylation but only up to the boiling point. The cloud point can then be increased by the addition of anionic surfactants which stabilise the solution [28]. Nonionic surfactants may promote chemical decomposition, crystal growth and reduce equilibrium exhaustion. CI Disperse Red 82 tends to grow agglomerates at the boil in the presence of 3 g l^{-1} fatty acid condensate or polyethylene glycol fatty acid ester. Nonionic surfactants act as levelling agents by solubilisation during dyeing with disperse dyes. It has also been reported that a nonionic agent accelerated desorption for 22 dyes out of 35 tested and in no cases accelerated absorption. Also, in 26 cases, the agent reduced absorption compared to that in the presence of only water. Thus it was concluded that the nonionic agent had a powerful retarding action. Ethoxylated nonionic auxiliaries can also be used as stripping agents after thermofixation dyeing with disperse dyes. They are added at high concentrations (200 g l^{-1}) to the pad liquor [45]. Dispersing agents should have a cloud point which is at least 5 – 10°C higher than the dyeing temperature to avoid precipitation of the dye [46].

Anionic surfactants produce foam and are relatively difficult to biodegrade. Nonionics, on the other hand, are less efficient, show no tendency to foam, and can be washed out easily from the fibres. Anionic surfactants with a linear structure are easy to biodegrade whereas branched chains are not biodegradable. Linearity of the chain also affects the biodegradability of the non-ionic surfactants [46].

Many commercial dispersing agents for disperse dyes are a mixture of nonionic and anionic products. The dye dissolves in the micelles formed by non ionic dispersing agents while anionic dispersing agents increase the cloud point of the system above the dyeing temperature[2].

2.2.5 Alkali-clearable Disperse Dyes

Alkali-clearable disperse dyes first came on the scene as a result of research by ICI in the 1970s on the dyeing of polyester cotton blends and discharge printing of polyester. Disperse dyes available at that time had a tendency to stain cotton during washing. Reduction clearing could not be carried out for all the cases as some of the reactive dyes used to dye the cotton were reduced under these conditions. This group of disperse dyes have ester groups in the side chain which are hydrolysed in the presence of alkali making the dye soluble and having no affinity for polyester. It was claimed that such dyes would overcome the problem of cotton cross-staining by disperse dyes during continuous dyeing or printing of polyester/cotton blends [6, 27, 47].

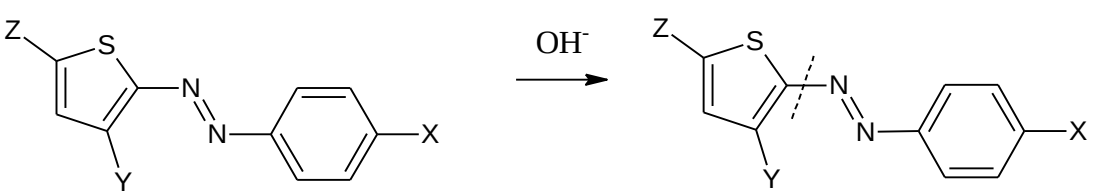


Water-insoluble, substantive

Water-soluble, non-substantive

Scheme 2.2 Mechanism of alkali hydrolysis of alkali-clearable disperse dyes based on azo-dicarboxylic acid

The first alkali clearable disperse dyes had two carboxylic acid ester groups in their structure which were converted into the water soluble alkali metal salt of the corresponding carboxylic acid on treatment with alkali as shown in Scheme 2.2.



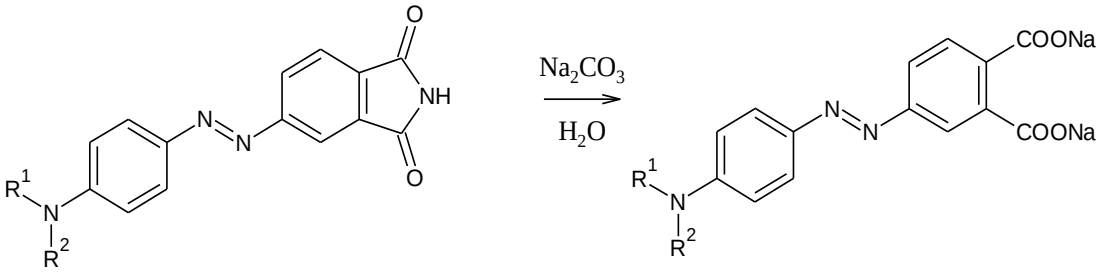
Water-insoluble thiophene disperse dye colourless product

Scheme 2.3 Degradation of azo-thiophene alkali-clearable disperse dye under the action of alkali [35]

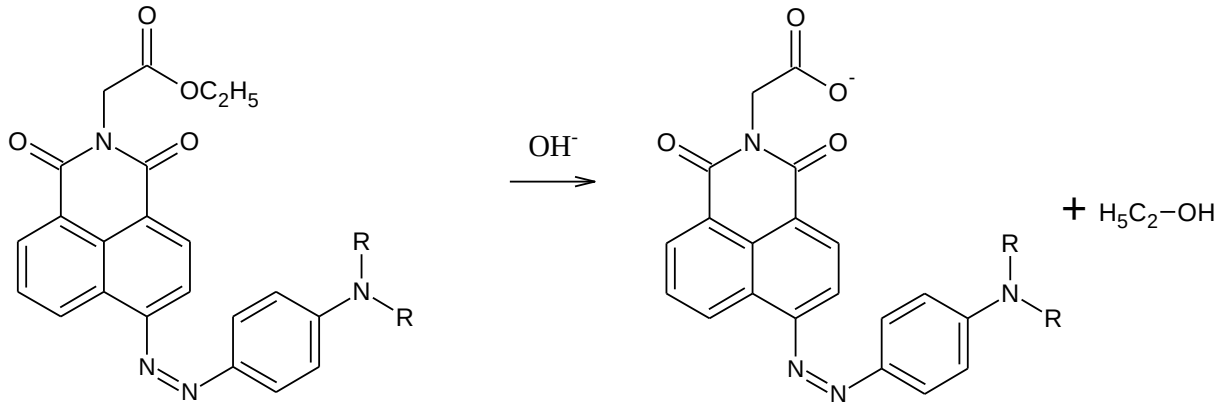
Further research in this direction progressed and dyes based on thiophene were developed and marketed. The presence of the thiophene structure makes the destruction of chromophore relatively easier as this group breaks down under the influence of alkali, and thus the dye is degraded into colourless or slightly coloured products whose structures are not identified as shown in Scheme 2.3 [35, 47, 48].

Disperse dyes based on benzodifuranone derivatives have excellent wetfastness and fastness to thermomigration. They also have good build up properties. The lactone ring of the benzodifuranone structure is easily hydrolysed conferring alkali-clearability to the dye [49].

Disperse dyes having phthalimide based structures, undergo ring opening and are converted to a water soluble product under alkaline conditions as shown in Scheme 2.4.



Scheme 2.4 Alkaline hydrolysis of an azo-phthalimide alkali-clearable disperse dye

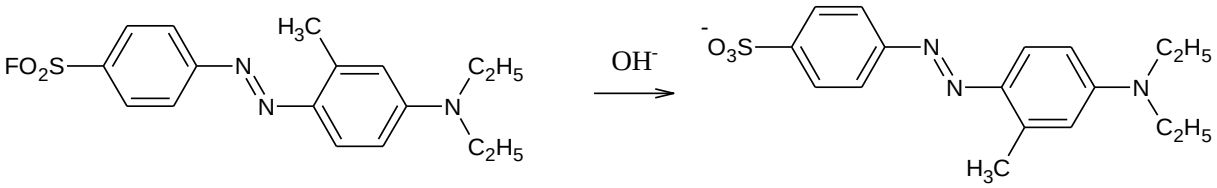


Scheme 2.5 Hydrolysis of N-ester naphthalimide based alkali-clearable disperse dye

Dyes based on monoazo–1,8-naphthalimide containing an ester group show alkali-clearability as shown in Scheme 2.5. Their washfastness properties after alkali clearing are inferior to the fastness properties obtained after reduction clearing [50].

More recently, alkali-clearable disperse dyes containing a fluorosulfonyl group have been reported. These dyes are hydrolysed by alkali without affecting the azo linkage as

shown in Scheme 2.6. These dyes showed good fastness properties after alkali-clearing when compared with reduction clearing. Analysis of alkaline hydrolysis kinetics show that below 90°C insufficient hydrolysis occurs. The dye also shows some instability at the pH used for dyeing. These factors need to be considered before such dyes can have commercial success [51].



Scheme 2.6 Hydrolysis of azo-fluorosulfonyl based alkali-clearable disperse dye

Alkali-clearable disperse dyes have the advantage that sodium dithionite is not needed during clearing, although the inconvenience of changing pH remains. These dyes are currently under a development phase and those which have already been marketed constitute only a small range [52].

2.3 Disperse Dyeing of Polyester

Dyeing is a process for the coloration of textile goods such that the colour imparted resists removal by various agencies, such as, water, light, laundering, perspiration and rubbing. In the process, dye molecules are dissolved in a medium from which they are adsorbed onto the fibre surface. The next step is the diffusion of the dye from the surface to the interior of the fibrous polymer and finally they are fixed in the interior by physical or chemical forces. From this description, it follows that the dyeing process is influenced by a number of factors and among these factors, the major ones are the fibre structure and properties, dye structure and the physical parameters required for dyeing. Polyester being a hydrophobic fibre which has only a limited number of polar groups and no ionisable groups, cannot be dyed with the traditional water soluble dyes which are ionic, have high relative molecular mass and are fixed to the polymer by physical forces or chemical reaction. The first factor in the dyeing is the dye-fibre affinity. None of the normal dyes used for the dyeing of other fibres, has any affinity for polyester. This is because of the non-ionic nature and the lack of any polar groups in polyester. Secondly, all the common commercial dyeing processes in current use involve the use of water as a transfer medium for the solid dye onto the fibre. Thus, the dyeing process is actually a competition between fibre and water for the dye [26].

Water, besides providing a medium for dye transfer, also often acts as a swelling agent with the application of heat, for natural as well as synthetic fibres. In the case of polyester, however, there is no swelling of fibre even at boiling. This is due to the extreme crystallinity and a high glass transition temperature of polyester. Finally, even if some dyes are able to attach on the surface of the polymer, they cannot diffuse further into the polymer and cannot form any type of bonds with the polymer. Thus, the dyeing of polyester during its development stage offered a multitude of difficulties at various levels. The first difficulty was overcome by the use of disperse dyes which were used for the dyeing of cellulose acetate. This is because cellulose acetate and polyester have some common properties such as hydrophobicity. Disperse dyes are nonionic molecules but possess some polar groups, for example, OH, NH_2, CN, NO_2. These polar groups impart a small but important solubility to the dye molecule and provide functional groups for bonding with the fibre. Thus, intermolecular forces between disperse dyes and polyester involve forces such as hydrogen bonding, π-π interactions, dispersion and polarisation forces. However, the disperse dyes used originally for cellulose acetate had only limited fastness properties on polyester. This drawback was overcome by modifying the chemical structure of disperse dyes for specific application on polyester. Disperse dyes are the only class of colorants which can be used to dye polyester besides the limited possibilities with pigments. The small size of disperse dye molecules make it possible for the molecules to enter into the polymer. As non ionic species, disperse dyes also possess affinity for polyester fibres. Besides disperse dyes and pigments, some specific vat dyes can be used to dye polyester as well [1].

The activation energy of a dye fibre system is the energy required by the dye molecules to move from the solution to the fibre. It varies with the dye and the fibres and is specific for each combination. The values for different dyeing systems are given in Table 2.1 [46].

Table 2.1 Activation energies of dye-fibre systems

Dye-fibre system	**Activation energy (kJ mol^{-1})**
Direct dye-viscose	59
Disperse dye-cellulose acetate	84 – 100
Acid dye-wool	92
Disperse dye-nylon	92
Disperse dye-polyester	126

It can be seen that disperse dyes on polyester have the highest activation energy which explains the level of difficulty for the dyeing of polyester [46].

2.3.1 Dyeing Methods

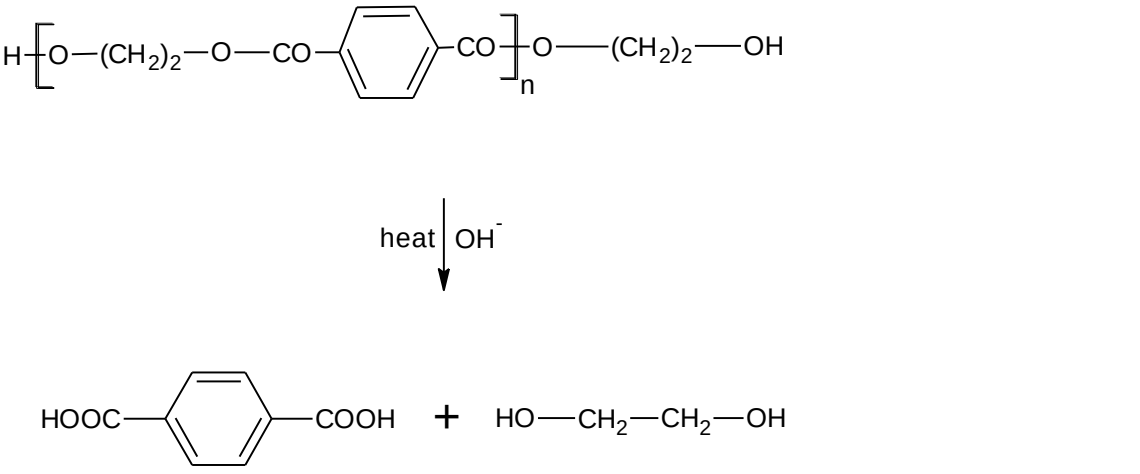
(a) Pre-treatments

As with dyeing of all fibres, a good pre-treatment of polyester is a prime requirement for the dyeing of uniform and level shades. Preparation of polyester fibres is fairly simple when compared with natural fibres. The basic objective of preparation is to remove contaminants so that they do not interfere with the dyeing and finishing processes. Synthetic fibres, generally, are free from natural impurities and, usually only a detergent wash at boiling is sufficient for the removal of production oils or size. Polyester fibres can be dyed in a number of forms and different forms need different preparation. Loose stock or raw stock has been given only a small amount of processing aids, most of which are self-emulsifiable. These forms can be dyed directly but a water rinse beforehand is generally beneficial. Knitgoods, yarns and woven goods need a preparation step before dyeing to remove oils, waxes, size and any cationic agents. Commonly, a treatment with 2 g l^{-1} of an anionic surfactant and sodium carbonate at 40 - 50°C is sufficient for scouring. Desizing is carried out for sized goods while a solvent emulsion followed by rinsing may be required for heavily oiled or waxed goods. It is imperative that no fibre lubricant is carried over into the dyeing bath.

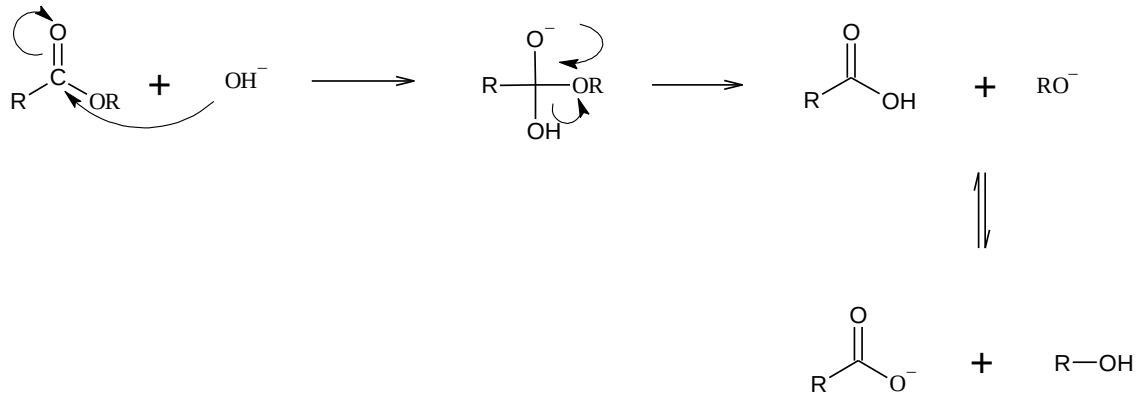
Singeing is the process of passing the fabric over a flame to burn the protruding fibres from the surface. Only polyester staple fibre fabric requires singeing while fabric composed of polyester filament does not need it. Singeing of polyester may produce bead like structures of melted polymer on the surface of polyester which are dyed differently from the fabric. These beads appear as spots after exhaust dyeing so singeing is done after the dyeing to avoid a spotty dyeing. However, this fault does not appear after thermofixation, so singeing can be carried out before the dyeing in this case.

Alkaline treatment of polyester fibres is an important stage before the dyeing process. This treatment involves the hydrolysis of the surface layer of polyester with sodium hydroxide. As a result, polyester fibres become thinner; their surface is roughened, leading to better tactile properties, dyeing properties, and better resistance to pilling and static electricity. This treatment makes use of the hydrophobicity and chemical inertness of polyester, which restricts the action of alkali to the surface only. Alkali saponifies the polyester on heating resulting in the formation of terephthalic acid and ethylene glycol according to Scheme 2.7(a). The reaction mechanism for alkaline

hydrolysis of a general ester is shown in Scheme 2.7(b). During alkaline hydrolysis, about 5 – 10% of the mass of the polyester is removed to achieve the desired properties mentioned above. However, hydrolysis has to be controlled strictly so as not to cause over reduction in the linear density of the polymer which can adversely affect the mechanical properties, such as strength and wear resistance of polyester [21].



(a)



(b)

Scheme 2.7 (a) Alkaline hydrolysis of polyester (b) Mechanism of alkaline hydrolysis of ester

Thermosetting or thermal stabilization is an important step in the preparation of thermoplastic polymer fibres. During thermal stabilization, the polymer is subjected to heating above its glass transition temperature and below the melting point. Under such conditions, the polymer undergoes changes in its morphological structure resulting in a decrease in the internal stresses which have been induced during previous processes, such as spinning, winding etc. This change in the internal structure affects the rate of dyeing where diffusion of the dye within the fibre is the rate determining step. Heat setting can be carried out before dyeing at the preparation stage or after dyeing as a part

of the aftertreatments. When carried out before dyeing, heat setting modifies the crystal structure of the polyester and thus the saturation values representing the maximum uptake of disperse dye. The amount of dye absorbed decreases with temperature, the minimum value being obtained at 180°C and then starts increasing again above 180°C [21]. Continuous yarn is heat set at 175 – 190°C for 20 - 30 seconds whereas staple fibre is heat set at 200 – 230°C for 5 – 30 seconds.

(b) Dyeing

Batch dyeing procedures can be carried out at the boil in the presence of carriers or under pressure at high temperature. Liquor ratio depends upon the dyeing equipment. Winch becks use a high liquor ratio 20:1 - 30:1, jet machines use 5:1 – 10:1 and package dyeing machines use 3:1 - 5:1. Continuous padding employs about 0.6:1 – 2:1 liquor ratio. Water quality is important for disperse dyeing as it is for all other dyes. Traces of soluble copper and iron can form co-ordination complexes with some disperse dyes resulting in shade change. Calcium and magnesium ions can react with anionic dispersing agents or levelling and wetting agents in the dye bath. For these reasons, chelating agents may be added to disperse dye bath, especially with problem-prone dyes. The pH is maintained between 4.5 – 5.5 to avoid dye hydrolysis. Nowadays, all commercial dyes have dispersing agents in their composition, which are added during the grinding process. The inclusion of dispersing agents in the commercial dyestuffs means that the dyer does not have to add dispersing agents while making dye solutions, except for special cases, such as for the dyeing of textured polyester. Anionic surfactants are added to improve wetting of the goods and also to stabilise the diluted dye dispersion. The stability problem is more of an issue with pale shades when the quantity of dye used is small. Non-ionic surfactants are used as levelling or retarding agents to ensure level dyeing. Surfactants generally create foam, unless defoaming agents have been added. Silicone derivatives are excellent defoaming agents but can form water resistant spots on the fibre [6].

In spite of having substantivity for polyester fibres, disperse dyes can only give pale shades under normal dyeing condition, that is, the boiling point of water at atmospheric pressure. For commercial dyeings, some other methods had to be devised. The very first approach to increase the rate of dyeing of polyester was to open up the internal fibre structure by the use of some swelling agents. These swelling agents or dyeing accelerants were called carriers. Thus polyester can be dyed at the boil in the presence of a carrier. Carriers are small molecular weight organic compounds which increase the

rate of dyeing of polyester with disperse dyes and thus polyester can be dyed in an open bath at boiling. Carriers generally belong to such classes as amines, phenols, aromatic hydrocarbons and esters. The most commonly-used carriers are *o*-phenylphenol, diphenyl and chlorobenzene. Carriers can be water soluble or non polar. They can act on the dye particles in dispersion and on the fibre. There are a number of theories proposed to explain the mechanism of carrier dyeing. One of these is that the carrier acts by increasing the water content of the fibre on absorption. The other is that carriers act as swelling agents for the fibre, thus improving the rate of dyeing. According to another theory, carriers plasticise the fibre which in turn decreases the glass transition temperature of the polyester making the dyeing possible at the boiling point of water [46]. However, carrier dyeing posed some problems. Most troublesome of these is the toxicity and odour of some carrier compounds. Since carriers are volatile compounds, there is a reasonable chance of their being condensed back onto the fabric producing stains, which are not easy to remove. In the case where some of the carriers are left on the fibre after dyeing due to inefficient removal, it can severely undermine the lightfastness of the goods. Thus, carrier dying is now mostly used for delicate fabrics such as polyester/wool blends [10].

A second approach used to increase the rate of dyeing was to raise the temperature to 135°C [5]. In the range 95°C to 135°C, an increase of only 4°C may double the rate of polyester dyeing [10]. Dye exhaustion is only about 10% at the boil and rises to about 80% in the temperature range 100 – 120°C and the remaining 10% exhaustion occurs between 120 and 130°C [46]. The increase in the rate of dyeing with the increase in temperature is due to two reasons. Firstly, this is due to the increase in the solubility of the disperse dye and secondly, due to the opening up of the internal structure of polyester. Diffusion increases and becomes important in the range 80 – 85°C, following the Arrhenius equation [3]. Dye molecules can migrate in any direction when inside the polymer structure. Although the preferred direction is along the concentration gradient, dye molecules can move to the surface of the fibre also [13]. Jet dyeing machines are mostly used for high temperature processes. This gives better exhaustion and improved fastness to light, rubbing and perspiration. However, high temperature dyeing has the disadvantage of giving rise to the oligomer problem. These materials appear as a white powder on the surface of the fabric and the dyeing machine. Oligomer deposits reduce the rubfastness, frictional characteristics in the case of yarns, and may promote the instability of dye dispersion. To overcome this issue, it is recommended to discharge

the dye bath at high temperature after the completion of dyeing. But this is not feasible in all cases, as such an arrangement requires a special machine for discharging the bath under high pressure. The use of cationic surfactants during disperse dyeing increases the oligomer content on the surface of the polymer, anionic surfactants decrease the content of oligomers while non-ionic surfactants disperse the oligomers almost completely in the solution. The efficiency of non-ionic surfactants to disperse the oligomers increases with the degree of ethyoxylation. The use of surfactants with a high number of hydroxyethyl units has a plasticising effect on polyester. However, adsorption of dye onto the fibre decreases [53].

A third approach is dry heating or thermofixation at 190 - 220°C; this method is used for continuous processing and is commercially known as the Thermosol process. Thermofixation makes use of the volatility of disperse dyes. Sublimed dye is in a monomolecular state [13]; disperse dye vapours are absorbed by polyester due to the substantivity. During thermofixation, the increase in temperature increases the volatility of the dye. At high temperatures, less volatile compounds transfer into the fabric but more volatile dyes are lost to the atmosphere [2]. Thus disperse dyes belonging to medium and high energy groups, which correspond to group B and group C are suitable for thermofixation. Group D dyes can be used but are not recommended unless excellent levels of sublimation fastness are required. They have a low diffusion coefficient and a higher temperature is required to vaporise them. The thermosol process is most popular for large yardages of polyester/cotton blends and only a small quantity of narrow width 100% polyester goods are dyed by this technique. In this process, the textile is padded with a dispersion of the dye, dried at about 90 – 100°C and then passed through a thermofixation chamber, which is in effect a dry heat chamber, at 180 – 220°C for 45 – 70 seconds. Since polyester has limited hydrophilicity it cannot take up dye easily during padding. However, when blended with cotton, cotton takes up the dye dispersion quite easily during padding and then the disperse dye is transferred from cotton to polyester during thermofixation. Transfer of disperse dyes from cotton to polyester during thermofixation occurs through the vapour phase and not by contact migration. Hence, the thermosol process is more suitable for polyester/cotton blends. However, all commercial reactive dyes undergo hydrolysis to a certain extent during their application to cellulose. If the hydrolysed dye is not removed, this causes poor fastness properties. Disperse dyes have a tendency to stain cellulose in blends but the dyes used for the dyeing of cotton do not stain polyester. The staining of cotton by

disperse dyes is minimum at the thermofixation temperature. However, the addition of urea and alkali required for the fixation of reactive dyes, increases the extent of staining [37]. The reduction clearing conditions which involve the use of caustic soda and a reducing agent may impair the brightness of viscose and hydrolyse the reactive dyes. Thus, polyester is dyed first followed by reductive clearing and cellulose is dyed afterwards [54].

2.3.2 Dyeing of Microfibres

As discussed in Section 2.1.4, a typical polyester microfibre has a count of 0.5 dtexpf. For a given count, microfibers have at least four times the surface area of a regular fibre. The processing of polyester microfibers involves some differences compared with the conventional fibres. A higher surface area results in more light being scattered, making the visual appearance of the dyed fabric lighter. Thus a higher amount of dye is required to obtain a shade on the microfibre than with regular fibre. Polyester microfibre fabrics are difficult to wet which causes problem in dyeing with regards to uniformity of shade [6]. The large surface area also results in a higher rate of dye adsorption and desorption. The dyeing rate has to be controlled very precisely to obtain level shades. A heating rate less than 1°C min^{-1} up to the dyeing temperature is used and also the cooling rate cannot be increased to above 1°C min^{-1}. Jet dyeing is suitable for polyester as it preserves the bulk and handle of the microfibres. Package dyeing is not recommended due to the obstruction of liquor flow as microfibres are denser and more compact. Crease inhibitors are frequently added. A greater amount of dispersing agent may be required to accommodate the higher concentrations of dye required. Lightfastness of microfibres is decreased due to more light being reflected from unit area. Washfastness is also affected because of the higher level of dye present on the surface. Because of their dense and compact structure, microfibres retain chemicals within their structure making their removal difficult. Thus the importance of reduction clearing for the removal of surface dye and oligomers is increased.

2.3.3 Dyeing Mechanism

Initial early research on the mechanism of disperse dyeing was carried out using cellulose acetate. Two theories were developed to provide an explanation. One is that the disperse dye is adsorbed on the fibre surface as a solid and diffuses afterwards by a solid state diffusion process in which the dye forms a solid solution in the fibre. The second theory states that the disperse dyes are transferred in a similar way to normal aqueous dyeing systems, from the very dilute solution of disperse dye which is present

in the dye dispersion. Bird (1954) first showed that disperse dyes have some solubility in water which can be increased by the addition of surfactants [28]. Bird, Manchester and Harris (1954) proposed that the dyes used at the time were bound weakly to the fibre by hydrogen bonding [55]. It was also demonstrated by Marjury (1956) that disperse dyes can transfer in the vapour phase [56]. This is the case during thermofixation and heat transfer printing when there is no water present. Disperse dyes sublime separating into single molecules in air before diffusing into the fibre.

Polyester is more hydrophobic than cellulose acetate, has a compact structure and is highly crystalline. The benzene rings of the terephthalate groups give rigidity to the amorphous zones resulting in a high glass transition temperature. Thus dyeing is carried out at a high temperature or in the presence of carriers at the boiling point of water. The saturation limit of the disperse dye on polyester increases with an increase in temperature while affinity decreases. Adsorption isotherms for disperse dyes on diacetate from the vapour phase are linear as is the case with aqueous dispersion. The dyeing process is exothermic similar to the dyeing of other fibres.

Disperse dyes are present in the fibre in the monomolecular form. On completion of dyeing, the dye on the fibre and in the dispersion is in a state of dynamic equilibrium. Disperse dyeing follows four stages; some of the dye from the dispersion dissolves to create a localised solution; the dye from the solution adsorbs onto the surface of fibre monomolecularly; more dye from the dispersion dissolves to balance the amount of dye which has moved onto the fibre surface; the dye from the surface of polyester diffuses into the polymer. The relatively hydrophobic crystals of disperse dye dissolve slowly in water and dispersing agents are used to improve dye solubility. The crystal form of the dye also has a significant influence on the solubility of the dye. The disperse dye dispersion is in an unstable state under dyeing conditions. Small dye crystals agglomerate to form large dye crystals which can then form aggregates resulting in the breaking down of the dispersion. Thus, care is taken during dyeing to complete the dye exhaustion before the dye dispersion is destabilised. Dye diffusion from the surface of polyester follows Fick's law, which states that the rate of diffusion of dye through unit area at any point in the fibre is proportional to the concentration gradient of the dye at that point. The rate of dyeing is not influenced by the concentration of the dye until the equilibrium is reached. Increasing the temperature has a twofold effect on the disperse dyeing. Firstly, it opens up the spaces in the interior of the polymer, making the dye diffusion easier. Secondly, the solubility of the disperse dye is increased at a higher

temperature. The dye solubility at 130°C is about 3.5 times its value at 95°C, which is roughly in the range 0.3 – 200 mg l^{-1} at 100°C and 0.6 – 900 mg l^{-1} at 130°C. Between 95 and 100°C, the rate of dyeing doubles for a 4°C rise in temperature [1].

The dyeing rate depends upon the diffusion within the polymer structure as this is generally the slowest step of all. This in turn depends upon fibre structure, dye structure and dyeing parameters. Since the glass transition temperature is a function of crystallinity, rate of dyeing is influenced by glass transition temperature as well. Manmade fibres have a relatively high negative surface potential, also referred to as zeta potential and this results in obstruction of dye adsorption and penetration. In the case of natural fibres, this potential can be overcome by adjusting the ionic strength of the dye solution [46]. Since disperse dyes are non ionic, the negative water-fibre boundary layer does not affect its adsorption and electrolytes are not required. In fact, electrolytes interfere with the negative charge on the surfactant particles surrounding the disperse dye and resulting in dye aggregation.

The effect of particle size on the dyeing behaviour of the dispersion has been studied. When the dyeing time was increased, the dye particles were observed to undergo a crystal growth resulting in a lowering of the solubility, thus reducing the maximum achievable dye uptake by the fibre. The dye solubility may be higher in very fine dispersions as small particles are more soluble than the large particles. Thus, a solution can be supersaturated with respect to large particles when small particles are present. Crystallisation occurs on the surface of the large particles resulting in an increase in mean size and a decrease in mean solubility. As a result, the limiting solubility decreases in a disperse dye bath and the dye uptake falls. To provide high fastness properties on polyester, disperse dyes of extremely low solubility have been designed. They are applied under high temperature conditions of about 130°C. However, the rate of crystal growth under these conditions is quite rapid and the solubility of the disperse dye falls at a greater rate than the adsorption by the polyester [56].

As explained in the previous sections, under practical dyeing conditions, there is a tendency for the larger disperse dye particles to grow at the expense of the smaller particles. This aggregation is favoured by the presence of electrolytes, high dye concentration, fast liquor flow and certain surface active agents. Aggregates are formed especially at 100 - 130°C and crystallise on the surface of the fibre [12]. Consequently the washfastness and rubfastness properties of the dyed textile are decreased.

In order to obtain level dyeing results, particle size and dispersion stability is very important. Ideally, a disperse dye should disperse rapidly when added to water and should give a fine dispersion of uniform particle size, less than 1 μm. Grinding of the dye particles to provide a small size increases the dyeing rate as there is an increase in the surface area. Dye uptake is also increased as the particle size of the dye is decreased. Apart from the uniformity of dye particles, the selection of appropriate dispersing agents is very important. Non-ionic surface active agents generally have lower cloud points. The dispersion must remain stable throughout the dyeing period and should not deteriorate in the presence of auxiliaries or at high temperatures [26].

There are a number of contradictory theories for the mechanism of carrier dyeing. The carrier can act in the dye bath as well as on the fibre. When interacting within the dye bath, carrier increases the dye solubility or forms a double layer on the fibre surface. This increases the concentration of dye in this layer and thus the dyeing rate is increased. Some carriers are useful for enhancing the rate of dyeing only; others influence the uptake of dye at the equilibrium while some are useful for both. Distribution constant is a measure of the relative amounts of dye in the fibre and dye solution at equilibrium and is used to assess the dye absorbed by the fibre. Diphenyl and chlorobenzene increase both the rate of dyeing and the distribution constant, whereas benzoic acid reduces the distribution constant but increases the rate of dyeing. Carriers with limited solubility in water but good solubility in fibre increase the distribution constant. Carriers with good solubility in water but lower solubility in fibre reduce the distribution constant. The action of carrier on the fibre can be explained by three theories.

1. Dragging theory. Carriers increase the water content of the fibre after adsorption due to the presence of –OH and $–NH_2$ groups. This also increases the amount of dye absorbed at equilibrium. This theory does not explain the mechanism of carriers devoid of such groups.

2. Swelling theory. According to this theory, carriers such as orthophenylphenol act by swelling the fibre. Again, this theory does not explain either the action of carriers which are not swelling agents or some swelling agents that do not act as carriers.

3. Plasticizing theory. As with plasticisers commonly used for plastic materials, carriers cause a relaxation of the internal tension in the fibre, shortening the fibre and modifying the microstructure. The glass transition temperature of the polymer is also decreased.

2.3.4 Fastness Properties

Disperse dyes show generally good fastness properties on polyester. However, there is a tendency for disperse dyes to aggregate (Section 2.2.3) and deposit on the fibre surface. If these deposits are not removed, they can adversely affect the brightness of the shade and wash, sublimation and rubfastness of the dyeing [14]. Disperse dyes give highest fastness properties to light when used on polyester and lowest on nylon. Lightfastness decreases as the depth of shade decreases. Nonionic UV absorbers can be added in the dyebath if excellent lightfastness is required, for example when needed for automotive fabrics [6]. All disperse dyes tend to migrate to the surface of the polyester during any heat treatment after dyeing. This migration depends upon the depth of the shade, temperature of the treatment and the properties of the dye. The migration is not due to the sublimation of the dye, although the least volatile dyes will generally produce the lowest level of surface deposits. If a softener film is present on the surface, this layer acts as a medium for disperse dye and the fastness to rubbing and dry cleaning is severely affected. The problem of surface deposits increases with deep shades. It is also observed that the tendency to produce surface deposits of dye reduces at high temperatures which are used in thermofixation. Wetfastness tests are generally carried out after reduction clearing and heat setting treatments. Fabrics are graded on the basis of the staining of the adjacent multifibre or nylon fibre. These ratings depend very much on the reduction clearing treatment as well as the heat setting treatment and any finishes applied [6]. During washfastness tests, which are normally carried out at temperatures in the range 20 – 60°C, it is improbable that the dye will diffuse out from the interior of the polyester. However, surface deposits of disperse dye which only loosely adhere to the fibre can produce staining of the adjacent fabric. Surface dye, as little as 20 mg kg^{-1} of the fibre, can produce significant staining of white goods. Even after a clearing treatment, dye may diffuse out of the polymer if polyglycol derivatives are applied as antistatic agents. The correlation between the amount of surface deposit of disperse dye and perspiration fastness or washfastness is only approximate. Also, the fastness ratings depend more on the solubility of the dye, and its affinity for the adjacent fabric [1]. The level of surface dye can be assessed by washing a weighed sample of the dyed sample with a non-penetrating solvent such as pyridine or cold acetone and measuring the absorbance of the resulting solution [9].

Sublimation fastness is a further important property of disperse dyes on polyester. Fastness to heat or sublimation and the rate of dyeing of disperse dyes depends upon the diffusion coefficient of the dye in the polymer. This factor in turn depends upon the relative molecular mass (rmm) and polarity of the dye molecule. The greater the rmm and the polarity of the dye, the higher will be its fastness to heat [30].

2.3.5 Thermomigration

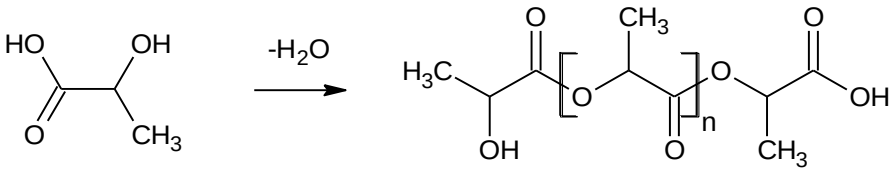
Thermomigration is the process in which disperse dyes move to a location where their chemical potential is low or from where they can evaporate. The chemical potential of disperse dyes is a function of their concentration. During dyeing, the initial rate of sorption of dye depends upon its chemical potential. Initially, the dye moves from a region of higher potential to lower potential, which is into the fibre. As equilibrium approaches, the potential difference between the two phases reduces and eventually it becomes zero. During levelling, the dye is desorbed from the locations of higher chemical potential and is redistributed to locations having lower chemical potential. Migration of disperse dyes takes place in the temperature range 110°C to 130°C.

Sublimation is also a migration effect by which disperse dyes can be absorbed or desorbed. Thermomigration can result in reduced wash and rubfastness. It has been indicated that even if the surface of the dyed polyester is cleared, it may show poor washfastness due to thermal migration. Migration of dye to the surface of the polyester increases when finishes are applied to the textile in which disperse dye can dissolve, especially on prolonged storage. These finishes include some lubricating oils, softeners and antistatic agents [1]. Thermomigration becomes an issue with the polyester cotton blends.

The degree of thermal migration is influenced by such factors as concentration of dye, temperature and time of heat treatment, concentration and type of finishes and the chemical nature of disperse dyes [13]. The thermal migration properties of a dye can be assessed by measuring the washfastness after heat setting. The results of studies show that there is little relation between the washfastness after finishing and the classification of the dyes with respect to energy level. Washfastness of disperse dyed goods is influenced both by the efficiency of the clearing process and the thermal migration properties of the dye [16]. Dyes based on the benzodifuranone structure are relatively less effected by the decreases in fastness due to thermomigration [35].

2.4 Poly (lactic acid) Fibre

As the name suggests, poly (lactic acid) fibre is produced from the polymerisation of lactic acid (2-hydroxypropionic acid) as shown in Scheme 2.8.



Scheme 2.8 Polymerisation of lactic acid into poly (lactic acid)

Lactic acid is produced by living organisms, including humans, during metabolism. It has been used in the manufacture of cheese, pickles, yoghurts, and food preservation. The raw materials for the commercial production of lactic acid are starch-containing plants such as corn, wheat, barley, sugar beets and sugar cane. However, petroleum, coal and natural gas can also be used as raw materials for the production of lactic acid.
PLA had been used in medical applications as biodegradable surgical sutures since 1950s. In textiles, it was first used in non-woven products. It is only quite recently that PLA has found new application areas such as apparel where it is used in blends with cotton for shirts, blouses, etc. The major advantages of PLA include the use of safer chemicals and processes in its production compared with other synthetic fibres as well as using renewable raw materials, and biodegradability [57].

Chemically, PLA is an aliphatic polyester. It is thermoplastic, with a glass transition temperature of 58 – 62°C and a melting point of 160 – 170°C [58]. As an ester, it can be hydrolysed easily. PLA has a low moisture regain 0.4 - 0.6%, which is slightly higher than PET. It can be dyed with disperse dyes and the recommended dyeing conditions are 110 - 115°C for 15 - 30 minutes at pH 4.5 - 5. However, disperse dyes exhibit different dyeing properties on PLA than polyester. Since, PLA does not have any aromatic structures, disperse dyes, generally, have poor intermolecular interaction with the polymer. Thus, disperse dyes give lower exhaustion on PLA. Despite having relatively poor exhaustion on PLA, disperse dyes have bright colours and higher colour yield on PLA than PET. The λ_{max} value of the disperse dyes on PLA shifts to a shorter wavelength than on PET [59].

2.5 Reduction Clearing

All textile dyeing processes are followed by a washing step at the end of the process whose purpose is to remove residual dye and other impurities from the surface of the dyed textile. Dyeing is a process used for the coloration of the textiles in such a way that the colour produced is resistant to removal by various agencies, which include washing, light and rubbing, to name a few. During dyeing, the dye molecules move towards the textile from the solution and diffuse into the interior of the polymer of which the textile is composed. In an ideal dyeing process, all of the dye molecules from the solution would exhaust onto the textile and will penetrate into the polymer structure. However, the principles of thermodynamics dictate otherwise. The movement of dye molecules from the solution towards the textile is a result of the concentration gradient between the two phases. Dye molecules move from a phase of higher concentration to that of a lower concentration. This movement continues until an equilibrium state is reached when the rate of movement of dye molecules into the textile and that of those moving out of it into the solution become equal. Commercially, all dyeing processes are stopped well before reaching this thermodynamic equilibrium [1]. Thus, at any time after the dyeing is stopped, there will be a number of dye molecules which have not yet penetrated into the textile polymer. Some of the dye molecules will be located on the surface of the textile and some of the dye molecules will be trapped in the spaces between fibres or yarns, depending upon the form of the textile. These loosely attached dye molecules are certain to come off later when the textile is used by consumers in everyday life. When this happens, the user, who is the customer, is likely to complain of fading of the textile or staining of adjacent materials occurring during laundering or even during wearing. This superficial dye may also impair the brightness of the shade [6]. The textile manufacturers, thus, understand the importance of the removal of the residual dye at the end of the dyeing process and the need for a washing or rinsing step carried out to remove this dye. In the case of water-soluble dyes, a simple aqueous wash-off may be sufficient for the removal of superficial dye molecules. However, in the case of water insoluble or dyes with limited water solubility, such as disperse dyes, aqueous washing is not sufficient [2, 60]. Also, disperse dyes particles tend to aggregate in dispersion as discussed in Section 2.2.3. Thus, these two characteristics of a disperse dye, namely limited water solubility and a tendency to form aggregates, make the removal of superficial dye particles difficult. In such cases a more rigorous washing off process using reducing agents is required to achieve optimum fastness properties. Beside the residual dye molecules on the fibre surface, disperse dyeing of polyester

presents another problematic issue to be solved, which is the presence of oligomers. Oligomers are small molecular weight polyesters, which are formed during the polymerisation of polyethylene glycol with terephthalic acid as discussed in Section 2.1.3. As the temperature is decreased after high temperature dyeing, oligomers migrate out of the polymer and deposit on the fibre surface due to their low water solubility. These surface deposits of oligomers are not dyed by disperse dyes and are firmly attached to the fibre and appear as white dusting powder on the machine parts. They also provide centres for nucleation of disperse dyes under favourable conditions thus destabilising the dispersion [14]. These surface deposits also affect the frictional characteristics of polyester yarns. These oligomers are not water soluble and a simple aqueous rinse is not an effective method for removal. Thus, disperse dyeing of polyester needs something more rigorous than a simple washing off to overcome these two problems. Reduction clearing is a powerful tool to remove these deposits. It is a washing process specifically designed to be carried out after the disperse dyeing of polyester to remove residual dye and oligomers from the surface. It involves treatment with an alkaline solution of reducing agent for 15 – 30 minutes at 60 – 80 °C.

2.5.1 Factors Affecting Reduction Clearing

An initial important parameter that influences reduction clearing is the form of the substrate, that is, whether the dyed textile is in loose fibre, yarn or fabric form. The deposited dye particles on the surface of the fibre severely undermine the brightness of the shade and the fastness properties of the textile. This issue is important for various types of substrate. However, in the case of loose fibre dyeing and package dyeing, the cleanliness of the fibre based on residual dye particles as well as oligomers becomes much more important. This is because fibre is spun after the dyeing of loose fibre while yarn needs to be rewound after package dyeing for further processing. Surface deposits of either dye or oligomers may create dust and increase the friction during these processes. In both cases, the surface requires to be extremely clean and even small amounts of dye or oligomers on the surface would create problems in subsequent processing, either spinning or winding. Thus, reduction clearing is normally carried out after dyeing of loose fibre and packages for all depths of shade [16].

A second important factor is the depth of shade applied during dyeing. Dye aggregation and deposition is increased as the concentration of dye used is increased. This in turn makes reduction clearing more important for medium and high depths of shade [10].

A third important factor is the dyeing method or the dyeing equipment used. In some instances, this is related to the form of the substrate. For example, loose fibre is commonly dyed in batches. Yarn can be dyed in package form or in hank dyeing machines. Package dyeing is particularly prone to deposition of dye because the layers of yarn act as a filter for dye particles. Fabric dyed in jet dyeing machines does not give rise to much problem with regard to surface deposits, as jet dyeing machines have an efficient rinsing system which is helpful in the removal of residual impurities [15]. However, when reduction clearing is carried out in partially flooded jet dyeing machines, excess sodium dithionite is required because of its reaction with air in the machine [3]. Fabric dyed on beams or using a thermosol process requires a rigorous reduction clearing step afterwards. Beam dyeing is similar to package dyeing of yarn in that the layers of fabric act as a filter for superficial dye and oligomers [16]. Thermosol dyeing, as discussed in Section 2.3.1, is a continuous dyeing method whereby fabric is impregnated with the dye solution and is passed through a thermosol chamber where dry heat in the region 200 - 220°C promotes the dye particles to migrate into the polymer in 45 - 70 seconds. In both cases, reduction clearing assists in the removal of deposited dye and oligomers from the surface, resulting in enhanced brightness of the dyeing and improvement in the fastness properties [61].

Another important factor regarding the importance of reduction clearing is the difference between laboratory and bulk dyeing processes. Generally, the washfastness and rubfastness of the bulk dyeings is lower than the laboratory dyed samples. In such instances, reduction clearing appears to be a process which can save the day for the dyer [62].

Since reduction clearing was introduced for polyester, its use on blends of polyester with other fibres complicate matters further. Generally, there are three reasons to blend different fibre types. These are to achieve economy in the process, to enhance functionality or aesthetics of the fabric [63]. Polyester is blended with natural fibres to enhance the functional properties of natural fibres as well as decreasing the product cost. Disperse dyes have a tendency to stain wool and this tendency increases with increasing fineness of the wool fibre [64]. Blends of polyester with wool necessitate a lowering of the temperature during reduction clearing to about 50°C so as not to damage the wool. Besides the lowering of temperature, milder alkali is used because wool is sensitive to alkaline conditions [17]. Although cotton in blends with polyester is not as sensitive to reduction clearing conditions, dyes used for dyeing cotton are often

reduced by the reducing agent. This is why, in spite of the higher cost and longer processing times of the two bath dyeing process, as discussed in Section 2.3.1, polyester cotton blends are dyed by thermofixation to achieve optimum fastness properties. It has also been discussed in Section 2.3.1, that disperse dyes have a tendency to stain cotton. In contrast, dyes used for dyeing of cotton do not stain polyester because of their hydrophilic nature as opposed to the hydrophobic nature of polyester. In the thermosol method, polyester is dyed first, followed by reduction clearing to remove the staining of cotton by disperse dyes and cotton is dyed afterwards. This sequence also ensures that reduction clearing does not reduce the cotton dyes [15]. Polyester elastane blends find wide applications in sportswear and swimwear. Elastane is a synthetic polymer consisting of linear macromolecules and at least 85% of segmented polyurethane. Elastomeric fibres can be stretched to at least three times their original length and can regain their original shape afterwards [19]. The glass transition temperature of elastane is below room temperature, in some cases even below 0°C. This increases the tendency of disperse dyes to stain elastane during dyeing of blends with polyester. Thus reduction clearing is essential to remove the staining of the elastane by disperse dyes so that optimum fastness properties can be acquired [65].

Poly (lactic acid) (PLA), which has been recently introduced as a biodegradable fibre, is closely related to polyester in terms of its chemical structure and, thus, is dyed with disperse dyes (Section 0). The biodegradability of PLA, which makes it much coveted for "greener textiles", confers on it sensitivity to high temperatures and aqueous alkalinity. Thus PLA is reduction cleared at lower temperatures of around 60°C using the milder alkali, sodium carbonate. Polyester microfibres on the other hand, require rigorous conditions of reduction clearing. It was discussed in Sections 2.1.4 and 2.3.2 that the diameter of microfibres is much smaller than regular polyester fibres. Thus, microfibres require a higher amount of dye to obtain a particular shade as compared with regular fibre. This leads to a higher level of dye deposited on the surface of the fibre at the end of dyeing. Also, polyester microfibre fabric has a densely packed structure which makes the washing off of unfixed dye more difficult, necessitating vigorous reduction clearing. Thus, higher amounts of reducing agent are employed for the reduction clearing of polyester microfibres [3, 23].

2.5.2 Mechanism of Reduction Clearing

Conventionally, sodium dithionite has been used as the reducing agent for reduction clearing of polyester, and thus it is used as the model reducing agent for the discussion on reduction of dyes in the subsequent text. Sodium dithionite is a strong reducing agent. It is commonly used in paper and rubber industries as a bleaching agent, besides textiles. In the textile industry, the largest use of sodium dithionite is for the vatting or reduction of vat dyes. Sodium dithionite is also referred to as sodium hydrosulphite and is commonly known by the brand name "hydros" in the industry. It is designated as CI Reducing Agent 1.

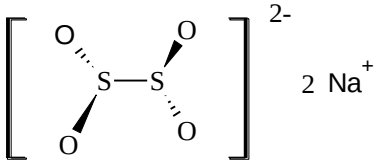


Figure 2.14 Chemical structure of sodium dithionite

The chemical structure of sodium dithionite is shown in Figure 2.14. The S-S bond length is 2.39 Å which is abnormally long when compared to the calculated bond length of singly bonded sulphur atoms (2.08Å). This long, and thus weak, bond confers strong reducing properties on sodium dithionite [66, 67].

A compound is said to be a reducing agent if it has the ability to lose electrons to another chemical species which is consequently undergoing reduction. Reduction is a chemical reaction in which a chemical species gains electrons. Since the gain of electrons by one species is concomitant with the loss of electrons by another, such chemical reactions are termed redox reactions. One of the species involved in the redox reaction undergoes reduction and the other undergoes oxidation. The species undergoing oxidation loses electrons and is acting as a reducing agent.

The reducing or oxidising ability of a compound can be described in terms of its redox potential. The standard reduction potential is defined as the potential difference in volts of a compound with reference to the reduction of hydrogen ions to produce hydrogen gas, which is set at 0 V at pH 0. The standard reduction potential of $[S_2O_4]^{2-}/2\ [SO_3]^{2-}$ is -1.12 V in an alkaline medium and -0.08 V in acid solutions ($[HS_2O_4]^-/H_2SO_3$) reacting according to Equations 2.1 and 2.2 [38, 68].

$$2[SO_3]^{2-} + 2H_2O + 2\,e^- \underset{\leftarrow}{\rightarrow} 4\,[OH]^- + [S_2O_4]^{2-} \quad (2.1)$$

$$2\,H_2SO_3 + H^+ + 2\,e^- \underset{\leftarrow}{\rightarrow} [HS_2O_4]^- + 2H_2O \quad (2.2)$$

The reducing ability of sodium dithionite depends upon the dithionite radical anion formed by homolytic cleavage of the S-S bond. The resulting free radical anion appears to be the initial transient species in the oxidation of dithionite and is in equilibrium with the dithionite ion as shown in Equation 2.3. The presence of dithionite free radical anion has been confirmed by electron spin resonance (ESR) spectroscopy [38, 67].

$$^{-}O_2S - SO_2^- \underset{\leftarrow}{\rightarrow} 2[SO_2]^{\cdot -} \quad (2.3)$$

An aqueous solution of sodium dithionite consumes oxygen dissolved in the water. When dissolved in water in the absence of oxygen, it decomposes into sodium thiosulphate and sodium hydrogen sulphite, at low pH (hydrolytic decomposition) or high temperature (thermal decomposition), according to Equation 2.4 [38, 67, 69].

$$2\,Na_2S_2O_4 + H_2O \rightarrow Na_2S_2O_3 + 2\,NaHSO_3 \quad (2.4)$$

In the presence of oxygen, an aqueous solution of sodium dithionite decomposes into sodium hydrogen sulphate and sodium hydrogen sulphite according to Equation 2.5. Sodium hydrogen sulphite and sodium hydrogen sulphate are acidic products and lower the pH of the solution [67, 70]. Thus, stock solutions of sodium dithionite are stored in an alkaline medium [16].

$$Na_2S_2O_4 + O_2 + H_2O \rightarrow NaHSO_4 + NaHSO_3 \quad (2.5)$$

Decomposition of sodium dithionite is influenced by changes in pH. A 0.0025 M solution of sodium dithionite undergoes the reactions given in Equations 2.6 – 2.9 within the temperature range of 0 - 32°C. The equations represent the reactions at varying values of pH from strongly alkaline for Equation 2.6, to neutral (Equation 2.7), to acidic (Equation 2.8), to strongly acidic (Equation 2.9). As the oxidation of sodium dithionite is exothermic, these processes are accelerated by an increase in temperature [16, 70, 71].

$$3Na_2S_2O_4 + 6\,NaOH \rightarrow 5\,Na_2SO_3 + Na_2S + 3H_2O \quad (2.6)$$

$$2\,Na_2S_2O_4 + H_2O \rightarrow 2NaHSO_3 + Na_2S_2O_3 \quad (2.7)$$

$$2H_2S_2O_4 \rightarrow 3SO_2 + S + 2H_2O \quad (2.8)$$

$$3H_2S_2O_4 \rightarrow 5SO_2 + H_2S + 2\,H_2O \quad (2.9)$$

Sulphite and hydrogen sulphite anions are in equilibrium with gaseous sulphur dioxide, again influenced by the changes in pH as shown in Equations 2.10 and 2.11.

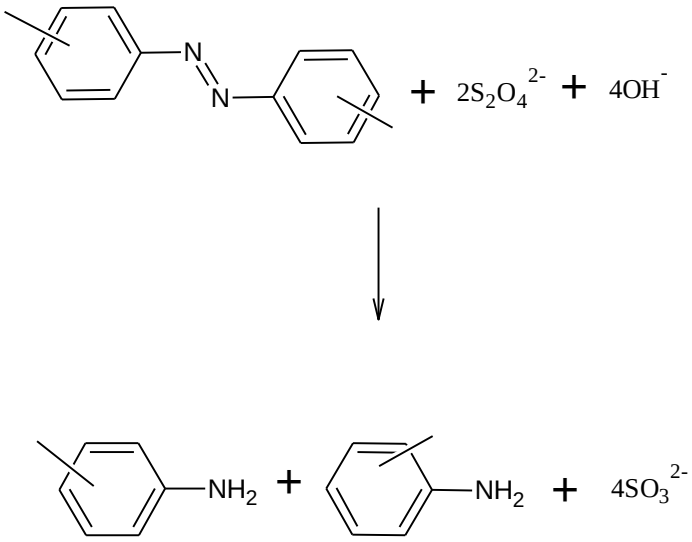
$$SO_2 + H_2O \underset{\leftarrow}{\rightarrow} H^+ + HSO_3^- \quad (2.10)$$

$$HSO_3^- + OH^- \underset{\leftarrow}{\rightarrow} H_2O + SO_3^{2-} \quad (2.11)$$

Sulphite ions have a catalytic effect on the decomposition of sodium dithionite. In the presence of oxygen, sulphite is oxidized to sulphate according to Equation 2.12. The standard reduction potential of this conversion is -0.93 V at pH 14 [2, 68].

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \qquad (2.12)$$

As discussed in Section 2.2.1, the majority of disperse dyes are based on the azo chromophore. Colour is a key characteristic of dye molecules and is due to at least in part, the presence of an extensive conjugation system in the molecule. A destruction of this conjugation system results in the loss of colour. This conjugation can be disturbed by either addition or removal of electrons. Reduction clearing makes use of the reducing properties of sodium dithionite for the destruction of the conjugated system of the dye molecules. Thus, dithionite reduces azo dye structures to colourless amines by providing electrons. According to Scheme 2.9, two moles of dithionite are required for the reduction of one azo bond [72].

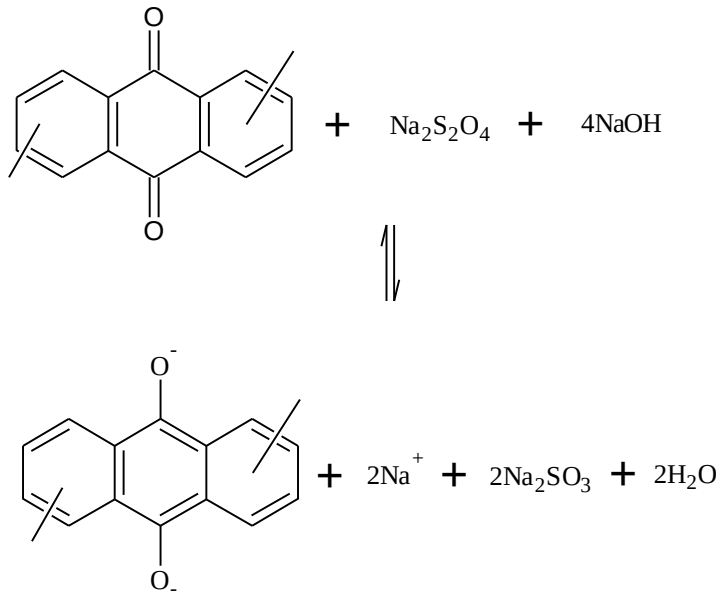


Scheme 2.9 Reduction of azo dye

The reduction of an azo dye is a four electron process occurring in two stages [73]. In the first step, a hydrazine is produced from which the dye then rearranges to produce amines [74]. Though the azo dye can be reduced in alkaline as well as acidic medium, the percentage of reduced products formed, that is, amines is higher in an alkaline medium while a lower amount of aromatic amines is generated in acetate buffer. This means that the presence of hydroxide ions has a pronounced effect on the cleavage of the azo dyes [75]. The ease of reduction of azo dye is influenced by the electron density around the azo group (-N= N-). Electron withdrawing groups at a para position to the azo group, decrease the electron density on the azo group, thus increasing its tendency

towards reduction and the formation of amines. The ease of reduction of azo dyes follows the order: hydrazone>azo>common anion. Nitro groups, if present in the dye molecule, are reduced more readily than the azo groups [7, 76]. Since sulphite ions have a tendency to convert into sulphate ($[SO_3]^{2-}$/ $[SO_4]^{2-}$), the sulphite which results from dithionite decomposition can also cleave the azo structures at high temperatures and alkalinity.

The reduction of anthraquinone dye by sodium dithionite is represented in Scheme 2.10. The mechanism of reduction of anthraquinone vat dyes by sodium dithionite involves initially the addition of dithionite ion to the carbon atom of a carbonyl group, which is relatively slow and thus the rate determining step. This is followed by a quick release of the sulphur-containing group from the adduct in the presence of hydroxide ions, with the retention of an electron pair on the oxygen of the carbonyl group [45, 77].



Scheme 2.10 Reduction of anthraquinone dye

$$Na_2S_2O_4 + 2NaOH + O_2 \underset{\leftarrow}{\rightarrow} Na_2SO_3 + Na_2SO_4 + H_2O \quad (2.13)$$

This model can be used to explain the reduction of anthraquinone disperse dyes by sodium dithionite. Thus, anthraquinone disperse dyes are reduced during reduction clearing into the leuco form which is solubilised in alkali and has no affinity for polyester [8]. Disperse azo dyes are reduced easily as compared with anthraquinone disperse dyes which require efficient rinsing after reduction clearing to prevent the re-oxidation by air back to the coloured anthraquinone structures [2, 6].

The significance of temperature selection for the reduction clearing process is that the residual disperse dye has to be removed from the surface without stripping the dye from

the interior of the polymer. The diffused dye molecules cannot move out of the fibre below the glass transition temperature of polyester fibre. Also the hydrophobicity of polyester retards the adsorption of any ionic compounds at this temperature. The temperature during reduction clearing is kept below the glass transition temperature of polyester but high enough for sodium dithionite to develop its reduction potential. In a study concerning reduction clearing of poly (lactic acid) fibre, polyester was reduction cleared with sodium dithionite and sodium carbonate at a temperature of 90°C for comparison purposes. There was no decrease in the colour strength of the dyed fabric and no dye stripping was observed. Thus, it appears that the upper limit for the temperature of reduction clearing is set by sodium dithionite as its stability is reduced at high temperature [8, 78].

Sodium dithionite reacts with oxygen in the air in such a way that 1.7 kg of sodium dithionite is consumed by 1 m^3 of air [11]. If the solution and air is kept still, the rate of decomposition depends upon the ratio of the exposed surface to the volume of the solution. Alkaline sodium dithionite when impregnated onto a fabric loses half of its reducing capacity on exposure to the atmosphere in one second. This initial rapid decomposition is then followed by a slower rate indicating that the initial high rate is caused by the oxygen absorbed in the fabric [45]. The time taken for half of the sodium dithionite to be oxidised is inversely proportional to the specific surface area of its solution. The specific surface area is the ratio of the surface area to the volume. The higher the specific surface area, the more rapidly the oxidation of sodium dithionite occurs. The oxidation is exothermic and as the temperature increases the rate of oxidation accelerates [9, 16, 79].

A surfactant, commonly non-ionic, is also used with reducing agent and alkali during reduction clearing. Its purpose is to help solubilise the reduction products and keep them in the dispersed phase. It also prevents the re-deposition of the degradation products on the fibre, easing their removal during subsequent washing [14].

2.5.3 Historical Significance of Reduction Clearing

The first reports of reduction clearing can be found in the 1950s when disperse dyeing of polyester started to develop. The traditional process is similar to the methods used today. It involves treatment with sodium dithionite as reducing agent, sodium hydroxide and a detergent between 70°C and 100°C for 15 minutes [80]. In some cases, reduction clearing has also been carried out at temperatures as low as 50°C [5, 81].

It was understood even at the time of its introduction that reduction clearing is a necessary evil which has to be carried out in some cases but should be avoided where possible. For example, Fern has suggested that reduction clearing can be disregarded when high temperature dyeing is carried out and sufficient time has been provided for the penetration of dye [61]. With the advent of modern high temperature dyeing machines offering an efficient rinsing system and the development of disperse dyes having good dispersion characteristics; the possibility was anticipated that reduction clearing might be dispensed with. However, the dyeing of polyester blends with natural and synthetic fibres still depends on reduction clearing to obtain acceptable fastness properties [15, 61, 64, 65].

Despite being carried out religiously in the textile industry, there has been surprisingly little research into reduction clearing. The general opinion about reduction clearing has been that it improves the fastness properties. Its impact on other properties such as effect on fibre strength and on the effluent from the process has not been studied intensively. The effect of reduction clearing on the fastness properties is well established especially for medium and dark shades, but it is carried out for most dyeings irrespective of their depth as it is important for the removal of oligomers [10]. There has been some related relevant research with reference to the reduction of vat dyes and more recently, in connection with the process development for poly (lactic acid) fibres. An important investigation into the use of various alternative reducing agents for the reduction clearing of dyed polyester was carried out by S. Anders. He compared sodium dithionite, formamidine sulphinic acid/thiourea dioxide (FAS/TUDO), hydroxyacetone, hydroxymethylsulphinate and an iron salt complex. The behaviour of these reducing agents was studied in the presence of air and in the absence of a textile sample. The treatment utilised 0.1 mol of each of the reducing agent at pH 12 using sodium hydroxide. The reduction potential of FAS/TUDO (-1040 mV at 80°C) was found to be the highest among the selected agents. Sodium dithionite was next with a redox potential of -900 mV, followed by hydroxymethylsulphinate which had a redox potential of -800 mV when used with anthraquinone derivatives as activator while hydroxyacetone had the lowest reduction potential of -480 mV. It was observed that sodium dithionite exhibited almost no increase in potential above 60°C; FAS/TUDO showed only a small increase while hydroxyacetone displayed a significant increase. In fact, hydroxyacetone showed a significant reduction potential only on reaching 80°C. Sodium dithionite and FAS/TUDO were compared in terms of their stability in the

absence of air at 60°C and pH 12. FAS/TUDO was consumed after one hour while only 10% of sodium dithionite had reacted. However, the quantity of FAS/TUDO used was half of the sodium dithionite. Fastnesses to alkaline and acidic perspiration of a black dyed polyester yarn with all the reducing agents were similar. However, fastness to washing was improved only by sodium dithionite and FAS/TUDO. The rest of the reducing agents could not improve the wash fastness properties even when applied at 100°C [11].

The effect of air content in sealed dyeing pots on the reduction clearing process of dyed PLA fabrics has been studied. It was found that the air content in the sealed pot can be decreased by increasing the liquor ratio. A lower content of air in the dye pot leads to better washfastness results even at comparatively low levels of sodium dithionite. The amount of sodium carbonate was varied to observe its influence on the washfastness properties. However, it was observed that increasing the amount of alkali did not have a significant effect on the washfastness properties of dyed PLA [82]. In another study, the effect of temperature on reduction clearing of PLA was investigated and was compared with its effect on polyester. Reduction clearing of PET with sodium dithionite and sodium carbonate did not produce any stripping of the disperse dye even at a temperature of 90°C [8]. PLA has been reduction cleared with sodium dithionite under acidic conditions; however, the improvement in the washfastness properties in an acidic medium was lower than in an alkaline medium [60].

2.5.4 Disadvantages of Reduction Clearing

The disadvantages of a process or of a substance can be studied from two perspectives. One is its influence on the process in which it is used and the other is on the environment. Reduction clearing does justice to the purposes for which it is used in polyester dyeing which are a brightening of the shade and improvement of the fastness properties of the dyed fibre. However, in terms of the other not so bright side of the picture, it creates a few problems. These issues are discussed below as its effects on the process and the environment.

a) Process

As the final stage in the dyeing of polyester, reduction clearing has two undesirable consequences which are the increase in process time and the increase in process cost. It may be concluded from the discussion given in the Section 0 that one of the major disadvantages of sodium dithionite is its extreme reactivity towards oxygen. This leads

to the need to use excessive amounts of sodium dithionite, in fact, more than the stoichiometrically required quantities. Disperse dyeing is carried out in an acidic medium due to the instability of certain disperse dyes in an alkaline medium and the tendency of polyester towards hydrolysis in an alkaline medium at high temperatures (Section 2.3). On the other hand, an alkaline medium is required for reduction clearing. Since the oxidation of sodium dithionite produces acidic products, excess alkali is required to keep the medium sufficiently alkaline [83]. After reduction clearing, the liquor has to be neutralised with an acid to avoid the danger of fibre damage which can be caused by alkali during storage. Thus the process entails two changes of pH, first from acidic during dyeing to alkaline for reduction clearing. Secondly, a change of pH is required from alkaline during reduction clearing to neutral in acid souring. This results in an undesirable increase in process cost and time.

b) Environment

The effects of reduction clearing on the aquatic environment are pronounced. The current focus on the effluent being discharged from the industries has led to the quest for environmentally benign processes and chemicals as well as the use of effluent treatment plants. The effluent should meet a number of criteria set by the government and environmental agencies before it can be discharged. A number of parameters such as dissolved oxygen, conductivity, total organic carbon and turbidity are used to check the influence of the discharged effluent on the aquatic environment. Biochemical or chemical oxygen demands are important parameters in this regard. Microorganisms in the aquatic system require oxygen for their respiration during which they break down the organic matter present in their environment into simple compounds. Such processes are termed aerobic processes and they involve degradation of organic matter by the microorganisms in the presence of oxygen to produce energy or to introduce carbon into their structure for their structural growth. A measurement of the dissolved oxygen content of the water is an indication of the activity of the microorganisms present. If there is a high load of organic matter, microorganisms consume a high amount of dissolved oxygen. This means that the aquatic life, for example fish, may suffer from a lack of oxygen. Chemical oxygen demand (COD) is a measure of the amount of oxygen required by a strong oxidising agent to oxidise the chemicals while biochemical oxygen demand (BOD) is a measure of the amount of oxygen required by the microorganisms to oxidise the organic matter present in that water. Chemical oxygen demand is measured by oxidising the sample of water with a strong oxidising agent,

potassium dichromate, in the presence of excess acid at high temperature. Biochemical oxygen demand is calculated from the difference in dissolved oxygen content of a sample before and after it is incubated in the dark under ambient temperature over a number of days, generally five. Sodium dithionite is an inorganic compound and is not biodegradable so the natural microorganisms present in the water streams do not degrade it. However, chemical oxidising agents are able to oxidise it. When discharged into effluent, the reduction clearing effluent causes a severe depletion of oxygen and an imbalance for the aerobic processes in waste water. The degradation products formed during reduction clearing include sulphites and sulphates from sodium dithionite and aromatic amines from azo disperse dyes. Sulphites can be oxidised to sulphates by hydrogen peroxide (Equation 2.12) but excessive amounts of sulphates can form hydrogen sulphide ions by anaerobic degradation which is eventually converted to sulphuric acid. This results in the corrosion of unprotected concrete pipes of the sewage system. Sodium dithionite also increases the content of sulphur in the effluent [12, 60]. As sodium dithionite is not biodegradable, its presence in the effluent increases the conductivity and COD of the water [9]. According to a study, the COD of a sample of effluent obtained after reduction clearing with sodium dithionite is 2715 mg l^{-1} and BOD is 650 mg l^{-1} (24% degradation) [10].

As with most other dyes, azo disperse dyes are biologically inactive. However, their reduction results in the formation of amines, some of which may be carcinogenic. Aromatic amines that have been classified as carcinogenic by International Agency for Research on Cancer include such compounds as benzidine, 4-aminobiphenyl and 2-naphthylamine. Exposure to benzidine can cause cancer of bladder and other organs. Some countries in the European Union have banned the use of azo dyes which might release the suspected carcinogens [34, 75, 84, 85]. The fragments of the reduced dyes may undergo additional structural transformations when discharged as effluent, resulting in the formation of products which may be more toxic [73]. Thus, effluent containing sodium dithionite needs treatment before it can be discharged into the streams, resulting in an increase in the process cost.

2.6 Organic Reducing Agents

Sodium dithionite has been the undisputed choice as a reducing agent in the textile industry for about a century. However, as the demerits of sodium dithionite were highlighted gradually, many alternative reducing agents came to light. Among these, derivatives of sulphinic acid and hydroxyacetone are the two important types of organic reducing agents which were able to compete with sodium dithionite at different levels. Sulphinic acid derivatives can be represented by the general structure shown in Figure 2.15. Generally, these compounds have good stability in air and their reduction potential is strongly influenced by temperature [60]. Hence, they are more suited for high temperature applications where sodium dithionite cannot be used.

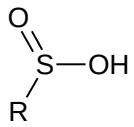
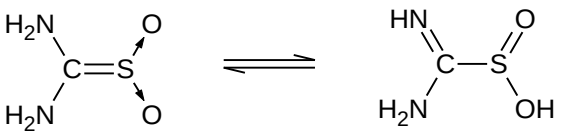


Figure 2.15 General structure of sulphinic acid

Two of the more important derivatives of sulphinic acid having applications in textile industry are formamidine sulphinic acid and hydroxymethane sulphinic acid.

2.6.1 Formamidine Sulphinic Acid

Formamidine sulphinic acid (FAS) or aminoiminomethane sulphinic acid is designated as CI Reducing Agent 11 and is more commonly known as thiourea dioxide (TUDO or TDO). As it is a derivative of sulphinic acid and is strictly not a dioxide, the more appropriate name is FAS. The compound exists in two tautomeric forms as shown in Scheme 2.11. It exists as structure A under neutral conditions which is similar to urea. It can be safely stored in this state as an aqueous paste at room temperature provided the pH is maintained at about 5. It has been marketed as Monofast in this form and was used for discharge printing [86].

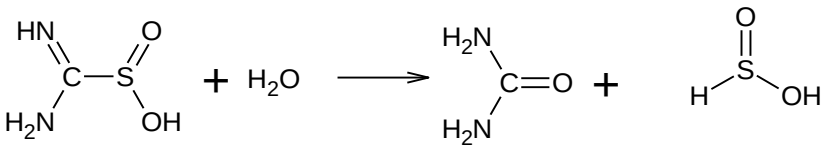


(A) (B)

Scheme 2.11 Tautomeric forms of formamidine sulphinic acid

The compound exists predominantly in the sulphinic acid form as depicted by structure B in Scheme 2.11, only in alkaline medium and develops reduction potential in this

form. The C-S bond in FAS is longer than in thiourea and thus this makes it a stronger reducing agent. On heating in an alkaline medium, FAS undergoes heterolytic cleavage of the C-S bond and is hydrolysed into urea and sulphinic acid (sulphoxylic acid) according to Scheme 2.12 [2, 14].



Scheme 2.12 Hydrolysis of formamidinesulphinic acid

Sulphinic acid converts to the sulphinate anion $(SO_2)^{2-}$ which exhibits strong reducing properties [11, 87]. The sulphinate ion reacts with the oxygen present in the system to form the sulphinate radical ion, sulphite radical and other reactive oxygen species along with other decomposition products finally leading to the formation of sulphate [69].

One of the major applications of FAS/TUDO has been in printing where it is preferred as a discharging agent for the printing of alkali sensitive fibres as it can produce reducing effects in mildly acidic to neutral conditions [32]. It has also been used for the reductive bleaching of wool as it does not damage wool like chlorine. It has not been a popular choice as a reducing agent in vat dyeing because of its higher reduction potential which may lead to over-reduction of some vat dyes. However, it may conceivably be more suitable for reduction clearing of polyester and in cleaning of machines than in vat dyeing [11, 88].

There are reports of using commercial products which are oxygenated derivatives of FAS/TUDO with alkali for reduction clearing at temperatures above 70°C for 1 – 10 minutes. Under these conditions sulphinic acid is produced which is a stronger reducing agent than sodium dithionite. This helps in the clearing of disperse dyes which are difficult to reduce with sodium dithionite [80]. When used for the reduction clearing of polyester dyeings, it was the only reducing agent among the five selected compounds which gave comparable washfastness properties to that given by sodium dithionite [11]. FAS/TUDO has also been used for the reduction clearing of PLA fabric under acidic and alkaline conditions. It was noted however, that it improved the washfastness properties of the disperse dyed PLA in alkaline medium only [60].

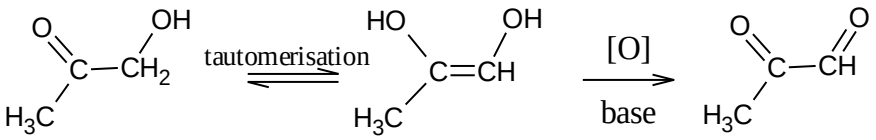
FAS/TUDO has a higher redox potential (-1100 mV) than sodium dithionite (-970 mV) and an equivalent amount of FAS exhibits almost twice the reducing effect of sodium

dithionite [11, 77]. FAS/TUDO has a lower equivalent mass than sodium dithionite and contributes less sulphur content to the effluent [4, 12]. It can be considered as of low toxicity due to its lack of mutagenic activity but there are conflicting reports about it [11]. However, it does give low BOD and COD values, about the same order as of sodium dithionite [60, 79, 89].

FAS/TUDO has been used as a reducing agent in the textile industry since 1950s. However, it has only found limited applications. The most important reason for this can be attributed to its high price [4, 11]. Another is that it decomposes rapidly in alkaline medium, even more than sodium dithionite, with or without oxygen thus posing problems in the preparation of stock solution [11, 12, 79]. Another reason which may have restricted the use of FAS/TUDO is its low solubility. It is only sparingly soluble in water having a solubility 37 g l^{-1} at 20°C [32]. There are also some concerns about the environmental effects of FAS/TUDO. These are raised due to a potential of release of urea from FAS/TUDO, about 0.6 lb of urea from 1 pound of FAS/TUDO [88]. This increases the nitrogen content of the effluent which may be objectionable in some regions [14]. FAS/TUDO may contain minute quantity of thiourea. Thiourea is carcinogenic and its level should be less than 1% in FAS/TUDO [11].

2.6.2 Hydroxyacetone

α-Hydroxyacetone (1-hydroxy-2-propanone) belongs to the group of compounds generally known as enediols. Enediols are generally low molecular weight species, consisting of two to six carbon atoms. Structurally they may exist as α-hydroxycarbonyl compounds, that is, they can be either α-hydroxyketones or α-hydroxyaldehydes. Such compounds exhibit strong reducing properties in an alkaline medium [78]. These are water soluble because of the presence of hydroxyl and carbonyl groups and having a low molecular mass. They exhibit keto-enol tautomerism as depicted in Scheme 2.13 for α-hydroxyacetone. The α-ketol forms of enediols are also referred to as reductones [90]. α-Hydroxyacetone is marketed as a liquid reducing agent for use in the textile industry with the brand name Rongal 5242 [12].



Scheme 2.13 Tautomeric forms of hydroxyacetone and its oxidation product

Since α-hydroxyacetone is a ketone, it exhibits a strong odour similar to acetone and its vapours are flammable. The reduction potential of hydroxyacetone is strongly influenced by temperature. At temperatures below 80°C, it does not show any significant reducing properties. At a concentration of 0.1 mol l^{-1}, α-hydroxyacetone has a reduction potential of only about -500 mV at 80°C and pH 12. However, it is quite stable under atmospheric conditions and is less sensitive to oxidation than sodium dithionite and FAS [11]. In the presence of 15 ml l^{-1} sodium hydroxide (38°Be), 5 g l^{-1} hydroxyacetone gives a redox potential of -810 mV at 60°C [14].

A major advantage of hydroxyacetone is that the effluent generated when it is used as a reducing agent is free from sulphate and sulphite salts. However, it increases the COD and total organic carbon content (TOC) of the effluent [4]. TOC is defined as the total amount of organic carbon, dissolved or particulate, present in the water. A high value of TOC indicates an increased activity of the microorganisms in the effluent which leads to a lower amount of dissolved oxygen, thus producing adverse effects on the aquatic life.

Despite leading to a high value of COD of the effluent, hydroxyacetone is considered superior to sodium dithionite regarding environmental effects because of its inherent biodegradability. However, it is possible to reduce the COD by treatment in a waste water plant.

Most of the research on the use of hydroxyacetone in textile processing has been carried out with regard to its use in vat dyeing. A number of patents have been published based on these studies [91-93]. In a comparative study of the use of sodium dithionite and hydroxyacetone as reducing agents for the indigo dyeing of cotton yarn, the COD of the hydroxyacetone effluent after treatment was only 1000 mg l^{-1} while the COD of sodium dithionite was about 8000 mg l^{-1} [11, 14, 94]. Recently, a comparison of the properties of sodium dithionite with a series of hydroxycarbonyl compounds, which included α-hydroxyacetone, in the reduction of indigo dye was reported [95]. It was shown that under the dyeing conditions used for indigo, sodium dithionite has higher reducing power than α-hydroxycarbonyl compounds. All of the selected reducing agents exhibited a rise is reduction potential with increasing concentration of sodium hydroxide and at a higher temperature.

The use of hydroxyacetone in the reduction clearing of disperse dyeing of polyester is reported rarely. In one report, it was shown that hydroxyacetone could not improve the

washfastness properties of a black disperse dyed polyester yarn [11]. Hydroxyacetone has also been used in a study on the reduction clearing of PLA with various commercially available reducing agents. However, hydroxyacetone did not have any effect on the washfastness properties of the dyed PLA. It should be noted that hydroxyacetone in this case was used at a temperature of 60°C to avoid the damage to PLA while the recommended conditions for reduction with hydroxyacetone are above 80°C [60].

It is likely that a major reason for hydroxyacetone having only a minor use in textile industry as a reducing agent can be attributed to its high cost [96].

2.6.3 Glucose

Glucose or dextrose belongs to the chemical class of compounds referred to as carbohydrates. The general empirical formula of carbohydrates is $C_x(H_2O)_y$. This chemical representation and the name carbohydrate indicates that these compounds were once thought to be hydrates of carbon. Contrarily, carbohydrates are polyhydric alcohols generally containing an aldehyde (H-CO-) or a ketone (-CO-) functional group in such a way that an oxygen atom is attached to each carbon atom [97]. Thus, all carbohydrates possess normally at least two functional groups, hydroxyl and aldehyde or ketone [90]. Carbohydrates are built of small units which are referred to as saccharides. Carbohydrates may be simple structures such as monosaccharides, disaccharides or complex large molecules which exist as polymers of monosaccharides and are referred to as either oligosaccharides or polysaccharides. Small molecular weight carbohydrates are more commonly known as sugars. Glucose is one of the simplest monosaccharides and has a molecular formula of $C_6H_{12}O_6$. It has high solubility in water in neutral medium, 817 g l^{-1} for anhydrous glucose [32]. It crystallises from aqueous solutions at temperatures below 50°C as α-D-glucose monohydrate and has a melting point of 80°C. Between 50°C and 115°C it exists as anhydrous α-glucose [98]. Since glucose has an aldehyde functional group it is referred to as an aldose. Aldoses are named according to the number of carbons in their structure. Glucose has six carbon atoms and is thus a hexose. The two names can be joined to describe glucose in one term as an aldohexose.

It is understood that an aldehyde and an alcohol may react to form a hemiacetal. This reaction can be catalysed by either acid or base. As has been described in the previous paragraph, glucose has two functional groups, an aldehyde and an alcohol. Thus, there

is a tendency for the two functional groups to react resulting in the formation of a hemiacetal. This hemiacetal can be formed in two ways. In the first case, the alcohol and aldehyde groups of two molecules of glucose can react intermolecularly to form a linear hemiacetal. In the second case, alcohol and aldehyde groups from one molecule of glucose can react intramolecularly to form a cyclic hemiacetal. The formation of a 5 or 6 membered ring structure is thermodynamically more favourable. Thus, glucose exists normally as a 6-membered cyclic hemiacetal consisting of a ring containing 5 carbon atoms and one oxygen atom. All the carbon atoms in the ring are bonded to hydroxyl and hydrogen groups except the 5th carbon atom which is attached to the 6th carbon atom outside the ring. Hence a more appropriate name for cyclic glucose is glucopyranose [97, 99]. The open chain and cyclic structures of glucose are shown in Figure 2.16.

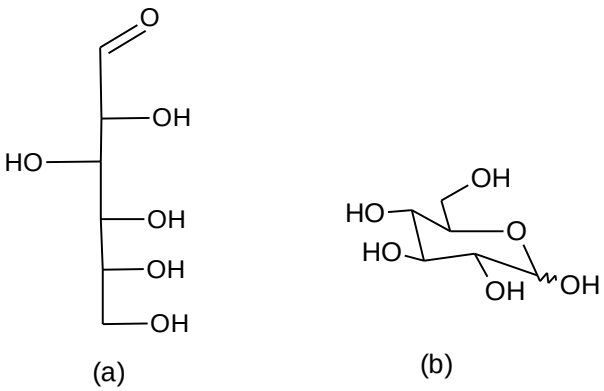
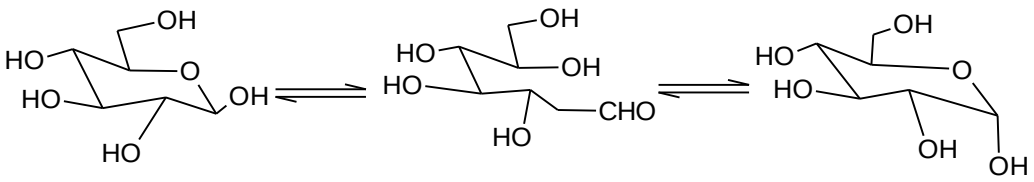


Figure 2.16 Chemical structure of glucose, (a) open chain form, (b) cyclic hemiacetal form

The cyclic glucose structure can exist in two isomeric forms depending upon whether the C-1 substituent is *cis* or *trans* to the C-5 substituent. α denotes the *cis* anomer while β denotes the *trans* anomer. In structural representation, the only difference between the two forms is the position of the hydroxyl groups relative to the first carbon atom. The α-isomer has the hydroxyl group situated below the carbon or in an axial position whereas the β-isomer has the hydroxyl group above the first carbon atom or in an equatorial position [97].

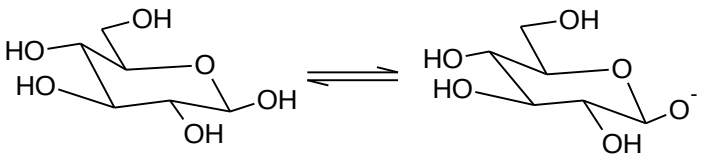
In weakly aqueous alkaline solutions, both α- and β-isomers of glucose can transform into each other to give an equilibrium mixture which has the two isomers in different proportions. This interconversion is referred to as mutarotation [32].



Scheme 2.14 Interconversion of the two anomers of glucopyranose

This interconversion of α- and β-glucose proceeds through the formation of the intermediate open chain aldehyde form of the glucose as depicted in Scheme 2.14. The equilibrium is established quite rapidly in acidic or alkaline medium and despite the quite low concentration of open chain aldehyde form, an aqueous solution of glucose gives characteristic reactions of an aldehyde such as the reduction of Fehling's solution or Tollen's reagent [2, 100].

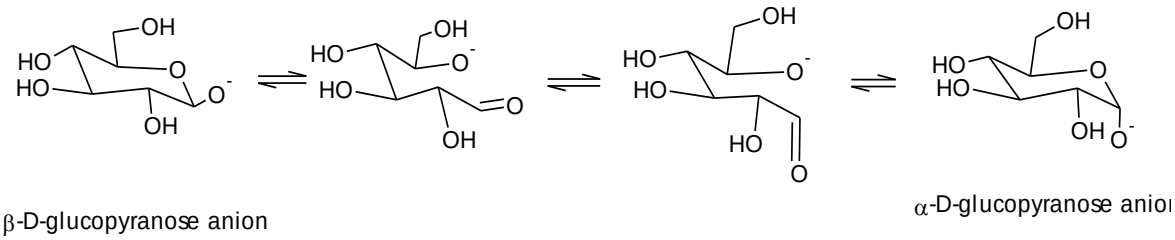
In an alkaline medium, glucose undergoes reversible as well as irreversible reactions. The reversible reactions include the ionisation, mutarotation and enolisation transformations. Glucose is readily ionised in an aqueous solution resulting in equilibrium of the neutral and ionised species as shown in Scheme 2.15. The ionisation of glucose implies that the anomeric hydroxyl (C-1) is ionised. The anomeric hydroxyl group is more reactive than the alcoholic hydroxyl groups [101]. The hydroxyl group at the anomeric carbon of the various cyclic hemiacetal forms of a monosaccharide is weakly acidic. The acidity of the monosaccharide depends upon the position of the anomeric hydroxyl group as well as hydroxyl group at the C-2. If the anomeric and hydroxyl group on the adjacent carbon atom have opposite configuration/conformation, the monosaccharide has lower acidity than when both the hydroxyl groups are in the same position, that is, both are axial or equatorial [102].



Scheme 2.15 Ionization of glucopyranose

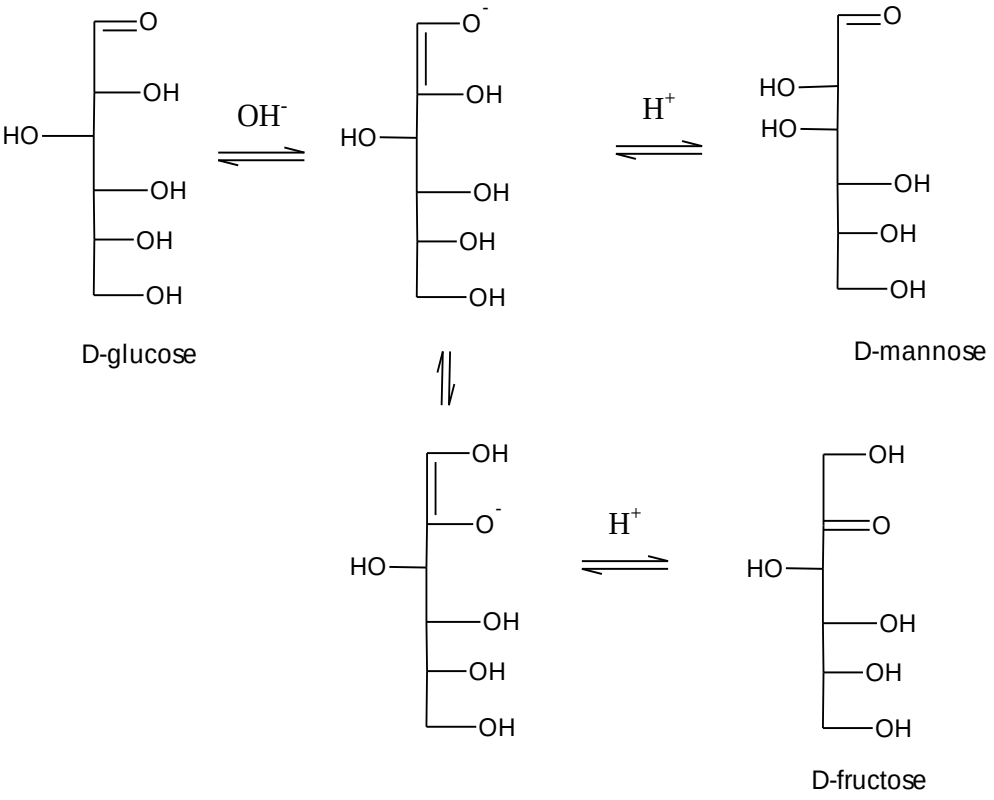
However, this cyclic ionised species is in equilibrium with the pseudocyclic/open chain form of glucose and is an intermediate in the mutarotation process.

As discussed in the previous paragraph, mutarotation involves the interconversion of different forms of cyclic hemiacetal, such as α- and β-glucose. Mutarotation of β-D-glucopyranose into α-D-glucopyranose is shown in Scheme 2.16.



Scheme 2.16 Mutarotation of glucopyranose

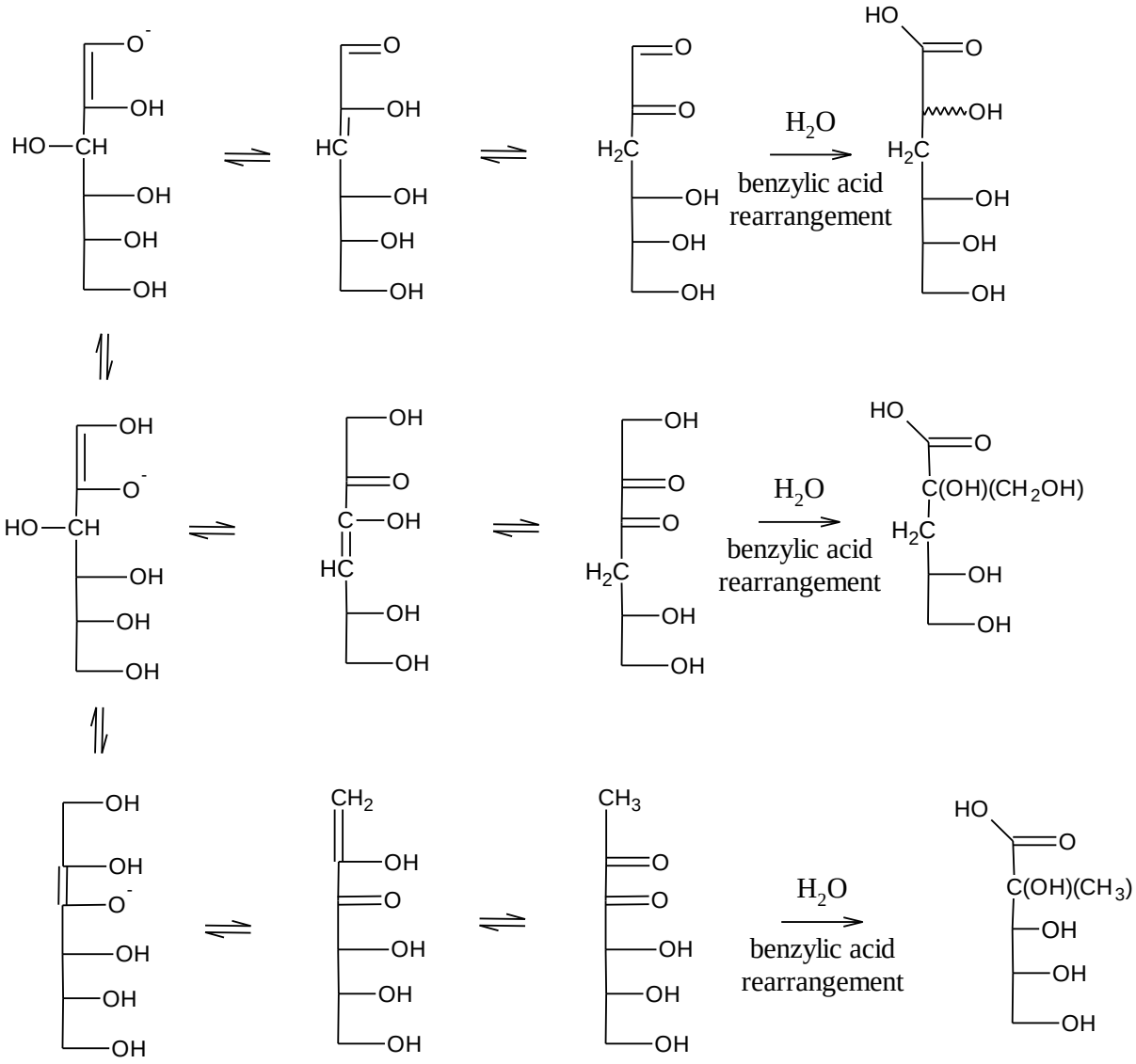
After ionisation and mutarotation, glucose then may undergo isomerisation, which involves the interconversion of different sugars such as glucose, mannose and fructose [103]. Scheme 2.17 shows the conversion of glucose into fructose and mannose [79]. It can be seen that isomerisation proceeds through the formation of an enediol ion.



Scheme 2.17 Isomerisation of D-glucose into D-mannose and D-fructose via enolisation

The irreversible reactions of glucose include alkaline degradation which also proceeds via enolisation. An enediol ionic species is considered to be the intermediate for the

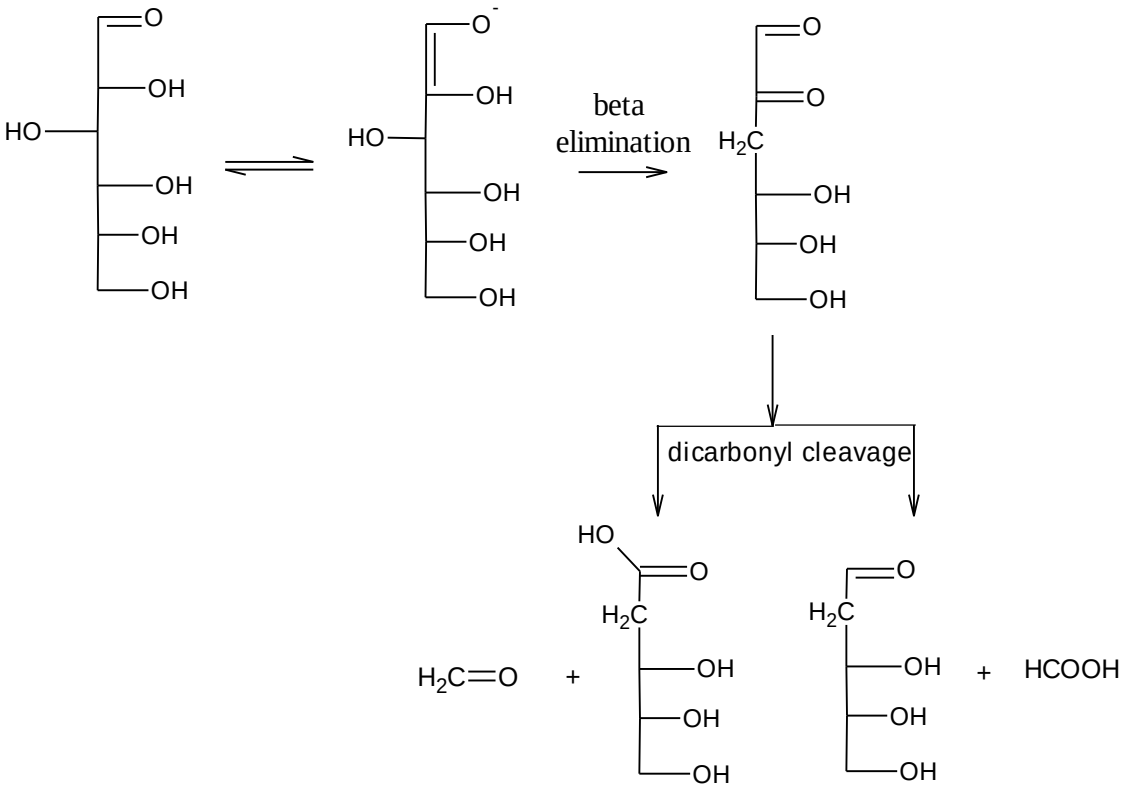
isomerisation and alkaline degradation reactions. Formation of an enediol ion is the rate determining step in these reactions which finally results in the formation of carboxylic acids through a number of reaction pathways. The enolate anion undergoes β-elimination to generate an α-dicarbonyl compound. The α-dicarbonyl compound then undergoes benzylic acid rearrangement to give α-hydroxycarboxylic acids or it undergoes cleavage at C1-C2 to give an aldehyde and a carboxylic acid [102]. The alkaline degradation reactions are in fact interconversion of C-2 to C-6 monosaccharides which are finally converted irreversibly into carboxylic acids as shown in Scheme 2.18 [79, 103].



Scheme 2.18 Alkaline degradation of glucose through benzylic acid rearrangement

Dicarbonyl cleavage of the intermediate species to produce an aldehyde and a carboxylic acid is shown in Scheme 2.19. Besides the carboxylic acids with 6 or less carbon atoms, a certain proportion of high molecular weight oligomeric products is also

formed during the alkaline degradation of glucose. These are most probably formed by the aldol condensation of smaller molecular weight products. These high molecular weight products consist of di-, tri- or poly-6-carbon sugar units. They also have conjugated enol structures and acidic character due to the presence of one or more carboxylic acid groups.



Scheme 2.19 Alkaline degradation of glucose through dicarbonyl cleavage

It has been postulated that the colour produced during the alkaline degradation of monosaccharides may be due to the presence of β-dicarbonyl structures in the oligomeric compounds. Hence, these oligomeric products may be the reason for the colour formation on degradation of glucose [102].

The rate constant for decomposition of glucose or hexoses in general is proportional to the hydroxyl ion activity and is dependent on the temperature. Other variables which influence the rate of decomposition of glucose are the type of alkali, concentration of glucose and the nature and pressure of the gaseous atmosphere. However, the composition of the degradation product mixture remains the same on varying the temperature. The concentration of glucose, however, does influence the nature of the products formed. For example, dilute solutions of glucose result in the formation of carboxylic acid products with less than 6 carbon atoms whereas concentrated solutions

of glucose result in the formation of carboxylic acid products with greater than 6 carbon atoms. All of the above discussion regarding the alkaline degradation of sugars refers to the reactions in which oxygen is excluded and conducted under a nitrogen atmosphere. In the presence of oxygen, products resulting from the cleavage of the C1-C2 bond are preferentially formed. The major products are formic acid and D-arabinonic acid (Scheme 2.20) while small amounts of D-erythronic acid, D-glyeric and glycolic acid are produced.

$$C_6H_{12}O_6 + O_2 \xrightarrow{OH^-} CH_2OH(CHOH)_3COOH + HCOOH$$

Scheme 2.20 Oxidation of glucose

The concentration of alkali also affects the nature of the degradation products. For example when the concentration of alkali is 0.5 N or higher, the major products of the oxidation of glucose are lactic and saccharinic acid with some small amounts of dihydroxybutyric acid and a resin which causes the solution to turn darker. When the concentration of alkali is decreased, higher amounts of volatile acids, formic and acetic acid, and resin are produced. The degradation of glucose into lactic and saccharinic acid is also suppressed in the presence of oxygen at atmospheric pressure while isomerisation and degradation is minimised under high oxygen pressures [100].

It becomes clear from the above discussion that the reducing action of glucose is due to the intermediate species formed during its oxidation or alkaline degradation. Although a number of intermediate species are formed, the common feature among these different species is the presence of the enediol structure which is known to produce a strong reducing action [90, 104, 105].

It was recognised quite early that glucose has reducing action due to the presence of the aldehyde group. The observation that it can be used to reduce aromatic nitro compounds was known as early as 1865. Galbraith et al (1951) used alkali and glucose to reduce aromatic sulphonated nitro compounds for the preparation of azoxy compounds [106]. In the textile industry, glucose has long been used as an additional reducing agent for the application of sulphur dyes particularly for the printing of sulphur black and with pre-reduced liquid brands [78]. There has also been some research on the use of glucose in indigo reduction [107]. Glucose has also been used with sodium dithionite for the reduction of vat dyes that are prone to over reduction. The addition of glucose acts as a stabiliser for sodium dithionite [4, 77]. Glucose is also used for partial stripping of indigo dyed denim to produce a washed and faded effect [108]. Besides

glucose, the use of other carbohydrates such as isomaltulose has been suggested for the reduction of vat dyes. Isomaltulose is a disaccharide of glucose and fructose. It reaches its redox potential equilibrium more rapidly than more common sugars [78, 109]. Glucose based products have also been used for the reduction clearing of disperse dyed PLA. However, there was no observed improvement in the fastness properties [60]. It should be noted that for the reduction clearing of PLA, lower temperatures are employed. However, glucose only develops a useful redox potential at high temperatures and under conditions of high alkalinity. In a study of glucose as a reducing agent for sulphur dyes, the reduction potential of the reducing bath was measured at the end of the dyeing. It was observed that at temperatures of 60 – 65°C, glucose showed a maximum reduction potential of -636 mV. The reduction potential did not rise beyond this value even on increasing the temperature to 80 – 85°C or by using higher concentrations of alkali [110]. Shah, in another study has also reported that the redox potential of glucose depends upon temperature and reaches a maximum at about 70°C [111].

The redox potential of glucose measured in alkaline solution may present difficulties in interpretation and may be open to misunderstanding. This is because the reduction potential of glucose is due to its complex set of degradation reactions and depends upon the alkalinity and temperature as well as the oxygen uptake [112].

The major advantage of glucose as a reducing agent is its biodegradability. The use of glucose in the dyeing of vat dyes is limited by the use of high temperature and alkalinity required to provide sufficient reducing power. However, anthraquinone and its derivatives can be used as accelerator in the process [104].

The problem with glucose is that it gives high values of chemical and biochemical oxygen demand. This is because of its biodegradability which means that it is a staple food for microorganisms. They readily digest it but inevitably this results in an increased consumption of oxygen leading to high values of BOD and COD. However, this issue can be addressed by the treatment of such effluent in aerobic waste water plants where glucose and its degradation products can be converted into gaseous by-products.

2.7 Electrochemical Reduction

It is well known that different types of energies can be converted into each other. The interconversion of chemical and electrical energies is studied under the branch of electrochemistry. Chemical energy can be used to produce electrical energy and electrical energy can be used to drive chemical reactions. The most common example of the former conversion is found in the batteries while the latter conversion is also widely employed in various industrial processes, such as electrodeposition.

It was discussed in Section 2.5.2 that redox processes involve the transfer of electrons between two species. The species which gives away electrons is the reducing agent and the one which accepts electrons is undergoing reduction. Since the reducing agent loses electrons in the process, it is said to be undergoing oxidation. Another approach to define redox processes is based on the change in the oxidation state of the substrate. The substrate whose oxidation state decreases is undergoing reduction and the one whose oxidation state increases is said to be oxidised. However, the net change in oxidation states of the reactants must be zero. Redox processes are reversible and always involve two species. Thus, it is not possible for a species to shed electrons unless there is some other species in its environment which can take it up. This is because electrons cannot survive in the solution on their own [38, 90].

Similarly, electrochemical reduction involves two species which are reducing agent and the species to be reduced/reductant. However, the reducing agent employed is not a typical chemical compound. Instead, a metal electrode is used as a reducing agent which acts as the source of electrons in this case. The substrate which is to be reduced acquires the electrons from the electrode instead of a chemical compound. Similar to chemical processes, electrochemical processes are influenced by temperature, pressure or concentration. However, an additional factor in the case of electrochemical reduction is the potential difference across the electrodes. This makes the process monitoring easier and more precisely controlled. An advantage of electrochemical processes is that the reaction does not require thermal energy and the reaction is feasible at lower temperatures. The major factor which has garnered the interest and attention of researchers is that all the products of an electrochemical process are regenerable and thus effluent load can be dramatically decreased. Currently, however, these advantages are offset by the high cost of the electrical energy required for an electrochemical process.

2.7.1 Theoretical Background

All electrochemical processes involve an electrolyte, an electrical circuit and at least two electrodes besides the analyte. This whole set up is referred to as an electrochemical cell. Since a redox reaction is a combination of two reactions, oxidation and reduction, the electrochemical cell is also composed of two half cells. Each half cell has its own electrode and electrolyte. The two half cells are connected through a salt bridge while an external circuit connects the two electrodes. The potential of each half cell can be measured and is depicted by positive and negative signs. In an electrochemical cell, the electrode with a positive voltage is the anode and the electrode having a negative voltage is the cathode. The cathode has excess electrons and acts as a reducing agent while the anode is deficient in electrons and thus acts as an oxidising agent. When an external potential is applied to the circuit, electrons move from the anode through the external circuit towards the cathode as an electric current. The charge/current then transfers from the cathode towards the anode through the electrolyte by ions, that is, negative ions move towards the anode and positive ions move towards the cathode. In this manner, the electrical circuit is completed and a current starts flowing from cathode to anode through the solution and from anode to cathode in the external wires. In this type of circuit, the voltage applied is limited by the electron transfer at the electrode-electrolyte interface. The electrochemical reactions take place at the interface between the electrode and the electrolyte as the electrons at the electrode-electrolyte interface are converted into ions and atoms. The thickness of the interfacial region is only about 1 nm and the solution beyond this interfacial region is not exposed to electrons. This interfacial region is better known as the electrical double layer [113, 114].

The potential of the half cell (E) is related to the concentrations of the oxidant and reductant by the Nernst Equation as shown in Equation 2.14. Here, O is the oxidised species or the one undergoing reduction and R is the reduced species or the one undergoing oxidation. E° is the formal potential of the redox couple. R is the gas constant, T is the temperature in Kelvins, n is the number of electrons transferred in the reaction and F is the Faraday constant.

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{[O]}{[R]} \tag{2.14}$$

The potential E is the measure of the ability of a compound to be oxidised or reduced in volts. The higher the difference between the positive potential and negative potential, the higher would be the voltage. The values of redox potential are helpful in making an estimation about the possibility of a reaction. For example, an oxidising agent has the possibility of oxidising another compound if the oxidising agent has a more positive redox potential. Thus, if a scale of redox potential values is considered, the compounds having a redox potential value to the right are oxidising agents and they can oxidise all the compounds on their left, while reducing agents have potential values lying on the left of the scale and they are able to reduce compounds which are on their right [32].

Electrode-solution interfaces can be classified as polarisable and non-polarisable. When the electrons can pass through the electrode-electrolyte interface easily, the electrodes are termed as non-polarisable. In this case, when the applied potential is increased, a concomitant increase in the amount of electrons passing through the electrode interface occurs without the excess build up of charge on the electrode surface. It can be said that a small change in potential leads to a significant increase in current flow. Polarisable electrodes are those which have a tendency to build up charge with an increase of applied potential as the movement of electrons through the interface is hindered. Thus a small change in current flow produces a significant change in electrode potential. An ideally polarisable interface is one where current can flow without changing the potential difference across it. No real electrodes behave as ideally polarisable in all circumstances but there are certain conditions under which a particular electrode and electrolyte combination behaves most closely to the ideal condition.

2.7.2 Cyclic Voltammetry

Various types of experiments are carried out to study the behaviour of current and potential in electrochemical redox processes. According to Ohm's law (V = IR), current and potential cannot both be controlled at a constant value simultaneously and thus there are three major types of experimental variation which can be performed.

1. Measurement of potential while the current is maintained at zero value.
2. Measurement of potential while controlling the current.
3. Measurement of current while controlling the potential.

The third type of experiment is referred to as voltammetry. Voltammetry involves experiments to study the relationship of current, potential and time. In voltammetry, application of potential produces a change in the concentration of the analyte and thus such experiments are said to be active experiments [115]. In these experiments,

potential can be scanned in directions either positive or negative of the reference point. When the potential is scanned in both directions completing a cycle, the experiment is referred to as cyclic voltammetry.

During cyclic voltammetry, the potential is varied linearly from an initial value (E_i) to a final value (E_f) which is also called the switching potential, at which point, the potential is then changed in the direction opposite to the initial potential as shown in Figure 2.17. According to the Nernst equation (Equation 2.14), the redox potential under non-standard condition (E) is related to the standard redox potential (E°) with a dependence upon the concentration of the reactants [116]. However, this relationship is valid only for equilibrium conditions, that is, when the rate of reduction of R (reduced species) into O (oxidised species) is the same as the rate of oxidation of O into R. It does not take into account the current flow in relating the electrode potential and reactant concentration [114].

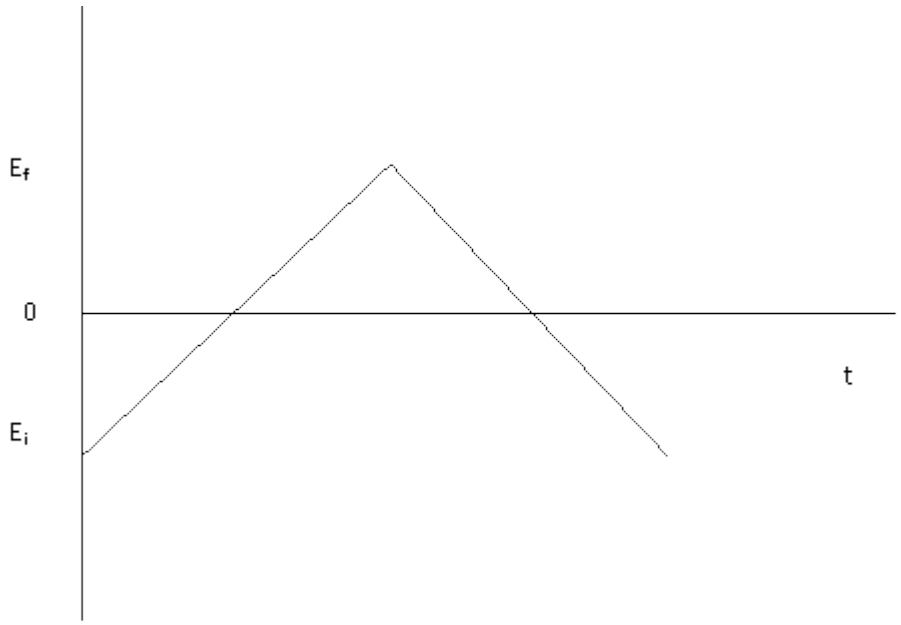


Figure 2.17 Variation of applied potential with time for a cyclic voltammetry experiment

The concentrations of the oxidised and reduced species in the Nernst equation refer to the concentration of these species at the electrode-electrolyte interface only. These concentrations may or may not be the same as the concentrations in the bulk solution. In the case where the concentration of the analyte in the bulk and at the interface are equal, there is no movement of ions due to the absence of a concentration gradient and hence no flow of current. There is a unique ratio of the oxidised and reduced species for

a particular solution where the current is zero. Generally, the concentrations at the interface and in the bulk solution are different and this difference is determined by the applied potential according to the Nernst equation. According to Fick's law, a species travels from a region of higher concentration to a region of lower concentration at a magnitude which is proportional to the concentration gradient. Thus, the oxidised form of the species (O) will move towards the cathode under the influence of the concentration gradient. On reaching the cathode, charge transfer occurs resulting in a change in the initial concentrations of O and R. This in turn increases the concentration gradient in the vicinity of the electrode and consequently the flux of O at the electrode increases.

Cyclic voltammetry is carried out under stationary conditions, as there is no stirring of the solution. The only type of transport from the bulk to the interfacial region or the electrode surface is by diffusion. The concentration gradient is smaller in the bulk solution and mass transport here is due to ionic migration. In electrochemistry, migration involves the movement of charged ions under the influence of electric field [113, 115]. As a result of the charge transfer at the interface between electrode and electrolyte, which are electron conductor and ion conductor respectively, and the mass transport in the bulk, a Faradaic current starts to flow through the cell. Faradaic processes are non-adsorptive in nature and the reactions are controlled according to Faraday's Law which states that the amount of charge that passes through the interface is proportional to the number of moles of the analyte converted. The electrodes where Faradaic processes occur are termed charge transfer electrodes since the extent of reaction depends upon the amount of charge that passes through them [113]. These current changes are plotted against the applied potential and the graph obtained is termed a cyclic voltammogram (CV).

A cyclic voltammogram gives important information about the rate of electrochemical reaction and the behaviour of a substance. Information such as the potential range within which the compound is electroactive, reduction potential, reversibility and number of electrons transferred, can be deduced from this graph.

The first important piece of information that a CV provides concerns the reversibility of the process. Different curves are obtained for electrochemically reversible, quasireversible and irreversible reactions. A typical cyclic voltammogram for a reversible reaction is shown in Figure 2.18.

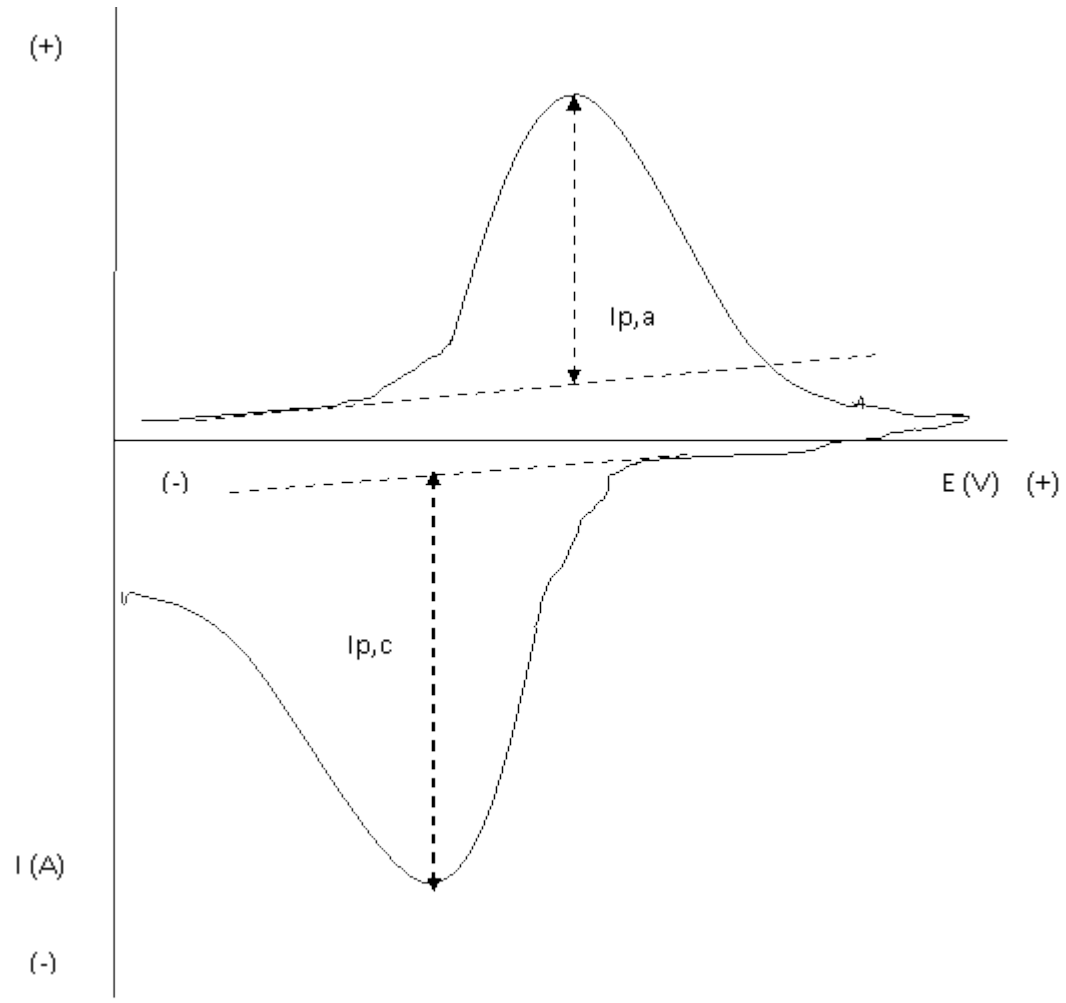


Figure 2.18 A typical cyclic voltammogram for a reversible reaction

Generally, the curve obtained has some peaks indicating the occurrence of electrochemical reaction at that voltage. The height and width of the peak are influenced by the concentration of the analyte, scan rate and the type of electrode. The shape of the curve also depends upon the transportation of the substance to the electrode. The peaks in the cyclic voltammogram show the potentials at which oxidation and reduction occurs. The peak on the right side or towards positive potential is the anodic peak where oxidation occurs and the peak on the left side or negative potential is the cathodic peak indicating the potential where reduction occurs.

The redox reaction taking place at the electrode can be described by Equation 2.15, where O is the oxidised state, R is the reduced state of the couple and *n* represents the stoichiometric number of electrons involved in the reaction.

$$O + n\,e^- \underset{\leftarrow}{\rightarrow} R \qquad (2.15)$$

Electrochemical reactions are considered reversible if the rate of reaction in both directions, forward and backward is high. This implies that the rate of electrochemical reaction at the electrode interface is higher than other steps in the reaction such as diffusion. In this case, the difference between the cathodic and anodic peak potentials as determined from CV is about 59/n mV at 25°C, where n is the number of electron transferred in the reaction. Also, the value of peak potential is independent of the scan rate and remains constant on changing the scan rate. However, practically, these conditions are rarely achieved [115].

When the solution contains both oxidised and reduced forms of the species, the midpoint potential is calculated by Equation 2.16.

$$E_{mid} = \frac{1}{2}(E_{p,c} + E_{p,a}) \quad (2.16)$$

In the case of a reversible reaction, the midpoint potential coincides with the half peak potential ($E_{p/2}$) which is the potential at which the current reaches half of the peak current value. Half peak potential or midpoint potential can be taken as equivalent to formal redox potential under most practical situations as it is assumed that the diffusion coefficients of both the oxidised and the reduced species are almost equal [117].

The values of cathodic and anodic peak currents can be measured directly from the CV as shown in Figure 2.18. The peak current value for a reversible reaction can also be calculated by the Randles Sevcik Equation (2.17).

$$I_p = 2.75 \times 10^5 n^{3/2} A D^{1/2} C^o \nu^{1/2} \quad (2.17)$$

Here, I_p is the current at peak maxima in amperes, *n* is the number of electrons transferred per molecule, A is the area of the electrode in cm^2, D is the diffusion coefficient in $cm^2\ s^{-1}$, C^o is the concentration of the bulk solution in mol cm^{-3} and ν is the scan rate in V s^{-1}. The peak height, which shows the maximum current, thus increases with the scan rate [115]. The ratio of the cathodic and anodic peak currents should be 1 for reversible reactions. Equation 2.17 can be thus used to calculate various parameters depending upon the parameters initially known [118].

Irreversible reactions are those where the rate of the reverse reaction is extremely slow and can be neglected. In such cases the peak voltage varies with the scan rate and the difference between cathodic and anodic peaks is greater than 200 mV. This is because the system is not in equilibrium. Also, the CV of an irreversible system does not have a reverse peak.

There is another type of electrochemical reaction intermediate between reversible and irreversible reactions which is referred to as quasireversible. Such reactions have a difference of greater than 60 mV but less than 200 mV between cathodic and anodic peaks.

The above discussion is appropriate for the diffusion controlled electrochemical processes. When the adsorption and desorption of ions from the electrode surface gives rise to a current due to charging of the electrical double layer, the process is said to be Non-Faradaic. Such processes are not diffusion controlled and may cause a change in the surface of the electrode which depends upon the applied potential or the concentration of electrolyte. The peak height and width in the CV are modified due to the presence of adsorbed species. If the adsorbed species have attractive forces between them, the height of the peak is increased and the width is decreased. On the other hand, if the adsorbed species have repulsive forces between them, the height of the peak decreases and the width increases.

Besides providing information about the charge transfer step of the electrochemical reaction, cyclic voltammetry is an important tool to diagnose the chemical steps which may follow or precede the charge transfer step at the electrode. An electrochemical reaction taking place at the electrode is heterogeneous. This charge transfer step can be coupled with a homogenous chemical reaction which may be reversible or irreversible. There are four categorizations of such reaction types [113, 117, 118]. The sequence of reactions is generally denoted as described below, using C for a chemical reaction and E for an electrochemical reaction

1. A chemical reaction precedes the reversible charge transfer step (CE). Both steps are reversible.
2. A chemical reaction follows the charge transfer step (EC).
3. Electrocatalytic reaction (EC′) where the chemical reaction (Equation 2.18) following the charge transfer step (Equation 2.19) regenerates the original electroactive species (O). Here, A and B are not electroactive in the specified potential range.

$$O + e^- \underset{\leftarrow}{\rightarrow} R \tag{2.18}$$

$$R + A \rightarrow O + B \tag{2.19}$$

4. ECE reaction when the chemical step is preceded and followed by a charge transfer step.

2.7.3 Instrumental Setup

A basic electrochemical cell can be operational with two electrodes, a supporting electrolyte and an external circuit. However, for precise control of potential, more than two electrodes, generally three, are employed. The electrical instrument which is used to connect and control more than two electrodes is a potentiostat [119]. The three electrode configuration is commonly used to minimise the solution resistance of the electrochemical cell. The three electrodes are reference, working and counter electrodes. In this system, potential is applied between the working and counter electrodes and measured between the working and reference electrodes. All of the current is diverted between counter and working electrodes by a high impedance reference electrode. The reference electrode is at a fixed potential so the potentiostat is used to monitor the voltage across the working electrode. When the potential across the working electrode is sufficient for a reduction or oxidation, current can be detected. The rate at which the potential changes, is kept constant for a cycle and is referred to as scan rate or sweep rate. Scan rate can vary from a few millivolts to 100 volts per second.

Generally the electrochemical cell is divided in two compartments, one housing the working and reference electrodes while the second compartment holds the counter electrode. By placing the reference electrode in close vicinity of the working electrode, potential losses due to solution resistance are minimised. The potential difference between the working and counter electrode is not generally measured but is adjusted so that the potential between working and reference electrode remains stable at the value specified by the user. A general circuit diagram for a three electrode cell controlled by a potentiostat is shown in Figure 2.19.

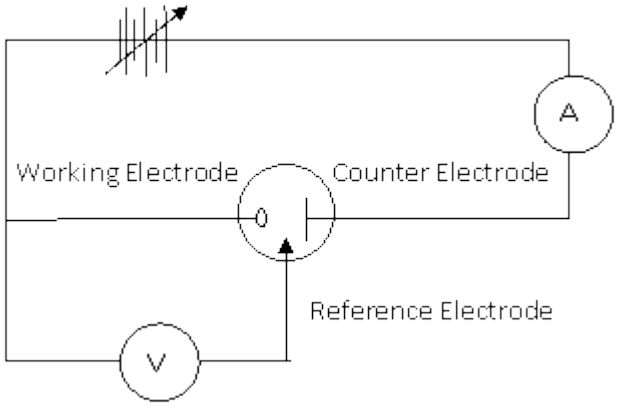


Figure 2.19 Schematic of a potentiostat circuit

The components of an electrochemical cell are described briefly in the following text.

Electrodes are the surfaces where charge transfer occurs between the analyte and the external circuit. The basic requirement for an electrode is that it provides current which is diffusion controlled. As long as the electrode fulfils this condition it can be of any shape, such as disk, cylinder or wire. Generally inert metals such as platinum and gold are commonly used as electrodes. These metals also provide ease of manufacturing for various types of electrode geometries.

A working electrode is the interface where the reaction under study occurs. These are sometimes also knows as indicator electrodes. The potential range within which an electrode can be used for measurements is called its working window. This is the potential range when it is polarized. An electrode is said to be polarized if the applied potential produces current due to electrical double layer charging only, that is, the current is due to a non-Faradaic process [113]. Electrodes can also be polarised due to the reduction of hydrogen. Electrodes at which reduction of hydrogen occurs at a more negative potential than is thermodynamically predicted are said to have high hydrogen overvoltage. Such electrodes include mercury and glassy carbon and act as good cathodes [120].

A reference electrode is used as a standard potential electrode against which the potential of the other electrodes is measured. The reference electrode must provide a stable potential at a certain temperature which does not change on the passage of current through it. It should provide reversible redox reaction and follow Nernst law. In contrast to a working electrode, a good reference electrode should be nonpolarisable and its impedance should be zero.

The standard hydrogen electrode is the primary reference electrode against which all other potentials are measured. It has a potential of zero volts when all the reactants have unit activity under conditions with unit value. However, a standard hydrogen electrode is not convenient to use as hydrogen gas has to be bubbled through it [113]. Other commonly used reference electrodes are Ag/AgCl and saturated calomel electrodes. The saturated calomel electrode is Hg/Hg_2Cl_2 in a saturated solution of KCl. The electrolyte in the reference electrode stabilises its potential and acts as a bridge between the analyte solution and the reference electrode. The electrolyte used in the reference electrode should not react with the contents of the electrochemical cell. Thus, an additional salt bridge is used to prevent direct contact of reference electrolyte and analyte solution. The ionic strength of the electrolyte in the reference electrode should

be about ten times that of the analyte. The electrolyte acting as a salt bridge should be compatible with the analyte and the reference electrolyte solutions. Generally solutions of potassium chloride, potassium nitrate, sodium sulphate or ammonium nitrate are used for the salt bridge. A drawback of the saturated calomel electrode is that it cannot be used at temperatures above 50°C due to instability of Hg_2Cl_2 [121]. When the concentration of ions is different or different ions are used for the electrolyte used in the reference electrode and supporting electrolyte in the cell, a potential difference arises due to the movement of ions across the salt bridge. This potential difference is known as the liquid junction potential and it can be minimised by selecting two electrolytes which have similar diffusion coefficients of ions [121].

In a three electrode cell configuration, the counter electrode or auxiliary electrode is used to provide a path for current. The potential between the counter and working electrode is not usually measured but it is controlled so that the potential between the working and reference electrode can be maintained at the specified level.

The supporting electrolyte provides conductivity for the flow of charge through the electrochemical cell across the two electrodes. It maintains a constant ionic strength and influences the electrical double layer which has a thickness of about 1 nm in the presence of sufficient supporting electrolyte. Supporting electrolyte is used at a concentration of about 100 times that of the electroactive species to mitigate the migration currents. Any strong electrolyte can be used as a supporting electrolyte provided that it is inert within the potential window of the redox system under investigation.

2.7.4 Methods of Electrochemical Reduction with Reference to Dyeing

Electrochemical reduction can be carried out by two methods, namely direct and indirect electrochemical reduction.

(a) Direct Electrochemical Reduction

As the name suggests direct electrochemical reduction involves a direct transfer of electrons between the electrode and the substrate at the electrode surface. In this method, the substrate molecules have to be in contact with the electrode surface for the transfer of electrons to take place. A number of techniques can be used for direct electrochemical reduction of dyes. One of these is reduction through a radical process. In this method, initially, some of the dye has to be reduced by using a soluble reducing agent such as sodium dithionite, to generate some leuco vat dye, such as in the case of

indigo dye. The indigo dye or pigment and leuco dye then undergo a comproportionation reaction to produce the indigo anion radical. This anion radical then acts as an electron mediator between the electrode and dye and the process thus becomes self sustaining. The electrochemical reaction rate is limited by the diffusion transport of the indigo anion radical and by a decrease in current density due to the liberation of hydrogen at potentials higher than -1100 mV [78, 122]. This technique has also been found to be successful for sulphur dyeing. However, a higher concentration of dye is required to obtain a specific shade due to the limitations associated with dye-electrode contact.

Another technique involving direct electrochemical reduction is of dye on graphite electrodes. The reactivity of a graphite electrode is associated with oxygen functionalities on the surface. The chemical activity of a graphite electrode can be enhanced further by the introduction of oxygen containing groups, for example introduction of anthraquinonoid structures as redox active molecules through covalent bonding with the graphite electrode for the reduction of indigo. Graphite electrodes are cheap and have a high surface area, and thus can be used to reduce vat dyes directly in aqueous suspension [78].

A major limitation of direct electrochemical reduction is the large area of cathode required. Since the dye has to be in contact with the electrode to allow reduction, a feasible dyeing can only be achieved if there is a substantial contact between dye molecules and the cathode.

(b) Indirect Electrochemical Reduction

In contrast to direct electrochemical reduction, the substrate molecules are not required to be in contact with the electrode surface for indirect electrochemical reduction. Instead, a chemical compound takes the electrons from the electrode and carries them over to the substrate molecule. This chemical compound acts as an electron carrier between the substrate and the electrode and is thus referred to as a redox mediator. Redox mediators undergo reversible oxidation and reduction. They are oxidised while reducing the substrate and the oxidised species are then reduced at the electrode to re-generate the original form and thus a cycle of reduction and oxidation ensues. The advantage of indirect electrochemical reduction is that the residual dye liquor can be recycled to generate the redox mediator which can be reused. In this situation, there are no decomposition products of the reducing agent [122]. However, the filtration and

concentration processes required for the recycling of mediator increase the cost and also pose some technical issues [78]. Another problem associated with indirect electrochemical reduction is that the dye reduction takes place in an electrochemical cell from where it has to be transferred into the dyeing machine. There should be bath circulation from the dyeing unit to the cathode so that the oxidised mediator can be taken to the cathode for reduction. The separator between the cathode and anode half cells, which ensures that the reduced dye is not oxidised at the anode, should have a small area. This minimises reoxidation at the separator due to the diffusion of oxygen. Re-oxidation at the separator is undesirable as it may cause a chemical short circuit which in turn necessitates a large area of the cathode to accommodate this. Thus, similar to the direct method, the electrochemical reduction of dyestuffs with mediators requires large amounts of electricity and a large cathode surface area to reduce the maximum amount of mediator. However, electrochemical methods enable monitoring of the reduction of dye by a measurement of the redox potential and the process can be controlled by the applied current [122].

2.7.5 Application of Electrochemical Reduction in Dyeing

In textile dyeing, both direct and indirect methods of electrochemical reduction have been proposed for the reduction of vat and sulphur dyes. As discussed in the previous section, direct electrochemical reduction involves the reduction of dye particles as a result of direct contact with the cathode surface. The two half reactions for dye reduction by direct electrochemical method can be written as shown in Equations 2.20 – 2.22.

Cathode: $$Dye + e^- \underset{\leftarrow}{\rightarrow} Dye^-$$ (2.20)

Anode, acidic anolyte: $$H_2O \underset{\leftarrow}{\rightarrow} {}^1/_2\ O_2 + 2\ H^+ + 2\ e^-$$ (2.21)

Anode, alkaline anolyte: $$2NaOH \underset{\leftarrow}{\rightarrow} {}^1/_2\ O_2 + H_2O + 2\ Na^+ + 2\ e^-$$ (2.22)

H^+ or Na^+ cations move through the membrane towards the cathode and oxygen is evolved at the anode. Reduction of sulphur dyes and indigo by catalytic hydrogenation has been described [83, 123]. However, this method is more suitable for use at the dye manufacturing facility for the production of pre-reduced indigo which is then transported to the dyeing facility.

In the indirect electrochemical process, the mediator compound is reduced at the surface of cathode by gaining electrons. The mediator then travels away from the cathode

surface into the solution towards dye particles and gives away these electrons to the dye molecule which is thus reduced. The mediator is oxidised in the process and then travels to the cathode surface to be reduced again. Thus, the cycle continues until all the dye is reduced. The electrode reaction and dye reduction in the bulk can be represented by Equations 2.23 and 2.24 where L is ligand, D is oxidised dye and D^- is reduced dye.

$$Fe^{3+}L + e^- \underset{\leftarrow}{\rightarrow} Fe^{2+}L \quad (2.23)$$

$$Fe^{2+}L + D \underset{\leftarrow}{\rightarrow} D^- + Fe^{3+}L \quad (2.24)$$

The ligand can either be triethanolamine or sodium gluconate or a mixture of both. Its function is to stabilize iron. It traps iron so that it cannot react with water. As compared to the direct method, indirect electrochemical reduction has been found to be more useful in textile dyeing applications.

2.7.6 Mediators used in Electrochemical Dyeing

Redox mediators which have been used for the reduction of dyes include iron-amine complexes [124, 125], iron-saccharic acid complexes, and some anthraquinone derivatives such as anthraquinone sulphonates and hydroxyanthraquinones [126-128]. An obvious but important pre-requisite for a compound to act as a mediator is that it is stable under the applications conditions. Besides that, a mediator should have sufficient negative redox potential at low concentrations. It should give comparable results in dyeing to that of conventional methods and produce reproducible dyeings. A mediator system should also have sufficient capacity to be used in industry. Mediator capacity is the stability of the potential produced in the bath and is expressed as the maximum cathodic peak potential. The reduction potential that can be used industrially is always close to the normal potential of the redox pair at normal rates of conversion. The mediator should also be regenerable with minimum cost of treatment [129].

(a) Inorganic Redox Systems

These are complex salts of metals with low valency. The most suitable salts are of iron. A number of ligands can be used with iron salts in the indirect electrochemical reduction method. These include such compounds as bicine and triethanolamine. A common characteristic of these ligands is that they possess the N-2-hydroxyethylamino group. The most important mediator is an iron-triethanolamine complex which gives a higher rate of dye reduction than sodium dithionite. It has a sufficiently negative redox potential (-1000 mV at about pH 13) to reduce vat dyes and produces reproducible

dyeing results that are comparable to that of sodium dithionite. However, its stability decreases as the pH drops to less than 13. The reduction of the iron amine complex is the rate determining step and its concentration is the limiting factor. The mediators are expensive but can be regenerated after dyeing [96, 122, 130]. The dyeing solution can be filtered after the process to regenerate the mediator which can be used again [129].

Iron can also be complexed with sugar acids such as gluconate. However, this system is more complicated than the iron-amine complex. This complex provides better stability at pH values around 10 but the potential that can be achieved is lower than the iron-TEA complex. Thus, mixed ligand systems of iron-amine-gluconate have been proposed to combine the pH stability and higher negative redox potential of both ligands [126].

(b) Organic Redox Systems

Indirect electrochemical reduction of vat, sulphur and indigo dyes with anthraquinone derivatives (monosulphonic acids, disulphonic acids, hydroxyl and other substituted products) as mediators has been reported [131, 132]. Most of the anthraquinone derivatives decompose at high pH values which are usually encountered in vat and sulphur dyeings. A number of stable dihydroxyanthraquinones have been studied as redox mediators for indigo. Among these, 1,8-dihydroxyanthraquinone, has shown the highest efficiency for indigo reduction [128]. Such systems have a cathodic peak potential of up to -850 mV vs Ag/AgCl/3 M KCl when used at a concentration of 1 g l^{-1} anthraquinone derivative and 4 g l^{-1} NaOH. However, these anthraquinone derivatives give a low rate of reduction at the cathode surface.

2.8 Enzymes

Enzymes can be defined at various levels, for example on the basis of their structure or on the basis of their function. Chemically, enzymes are proteins, and as such they are made up of amino acid residues which number from a hundred to several thousand resulting in molecular mass ranging from 1000 to more than 1,000,000 [14]. Functionally, enzymes are catalysts. Enzymes are secreted by living cells to catalyse numerous reactions in the living organisms. Since enzymes are the products of living cells and are used to maintain the metabolism of the living cell, they are generally referred to as biological catalysts, to distinguish them from chemical catalysts. The Nomenclature Committee of the International Union of Biochemistry and Molecular Biology on the Nomenclature and Classification of Enzymes (NC-IUBMB) has categorized enzymes into six types depending on the type of reaction that they catalyse.

The direction of the reaction which is being catalysed is also taken into account as all of the reactions catalysed by enzymes are reversible. Thus, all the enzymes in a class are classified on the basis of one direction of the reaction only, even if in some cases that direction is not observed practically. The naming of enzymes has been systemised, but the trivial names have commonly been retained as well [133].

2.8.1 Structure

The amino acid residues of an enzyme are connected through peptide bonds to form polypeptide chains. These polypeptide chains are folded in a specific order resulting in a three dimensional complex. The sequence of amino acids is different for various enzymes and specific amino acids occupy specific strategic positions in different molecules. The three dimensional physical structure of enzymes confers characteristic properties on enzymes. Thus, the specificity of enzymes, that is, their property to act on a specific substrate even when various types of substrates are present, is due to this structure. The enzyme may be a simple protein or it may also contain a non-protein unit. The latter types are referred to as conjugated proteins. This non-protein moiety may be an organic (for example carbohydrate) or an inorganic (metal) component. The function of the non-protein component may be to provide structural stability or it may provide catalytic activity to the enzyme. The three dimensional structure of enzymes also creates the active site where the substrate-enzyme interactions occur. An enzyme can have more than one active site.

2.8.2 Mechanism of Action

Enzymes are catalysts which increase the rate of an otherwise slow reaction by about a thousand times. Enzymes are able to achieve this by the lowering the activation energy of the reaction. The enzyme-catalysed reaction does not have a different free energy change and the total change in energy of the uncatalysed and catalysed reaction remains the same. It is postulated that the enzyme binds the substrate to its active site to form a transient species. The active site of an enzyme is a three dimensional hole in its structure. The binding of the substrates is influenced by the shape and configuration of the enzyme. The coiling and folding of the polypeptide chains allows the reactive groups which are not adjacent to each other in the structure to come closer [133]. The binding of the enzyme and substrate had been described by the lock and key model initially but lately a new theory known as induced-fit model has found more acceptance. The enzyme will bind to a substrate only when it is complementary to it. When the substrate is bound to this active site the reactive amino acid groups of the enzyme can

interact with the substrate more efficiently and the intermediate transient species formed in the presence of enzymes is more stable [133]. The substrate then undergoes chemical changes resulting in the formation of products after which the substrate and products are released from the enzyme-substrate complex. Thus, the enzyme retains its activity and is not consumed in the reaction.

2.8.3 Properties

Since enzymes are proteins, chemically, they exhibit properties typical of the molecular features of the amino acids. Enzymes can behave as an acid or a base depending upon the pH. At a certain pH, the isoelectric point, the enzyme exists as a zwitterion and has no net charge. Enzymes have very specific action, in that they only interact with the substrate for which they are designed. The specificity of an enzyme is so sharp that, for example, it can distinguish between the different isomers of a substrate and catalyse the reaction for one specific isomer only [14].

2.8.4 Enzyme Activity

The activity of enzymes is different from their protein content. Different methods are used to determine the enzyme activity under certain conditions. These methods are referred to as enzyme assays. The activity of an enzyme is measured in katals. One katal is the amount of enzyme which is utilised in the transformation of one mole of substrate per second under standard conditions of temperature and pH. International units have also been used for the measurement of enzyme activity. One international unit is defined as the amount of enzyme used to transform one micromole of substrate per minute [134]. The two units are related to each other by the expression, 1 IU = 16.67 nkat [133].

The activity of an enzyme is an important property which has to be controlled to use the enzymes successfully in any application. All external parameters, such as temperature, pH and time, affect the activity of the enzyme which is, in turn, governed by the structure of the enzyme. Enzymes can function properly under the ambient conditions in the living cells which are much milder than those encountered in normal synthetic chemical reactions. Although, the exact values of temperature and pH vary for individual enzymes, at extremes of temperature and pH, the three dimensional structure of enzyme is disturbed resulting in a loss of its catalytic activity. The optimum pH range for an enzyme to provide maximum activity is influenced by the acid-base behaviour of both the enzyme and the substrate. When there is a change in the acid-

base behaviour of the enzyme, the electrostatic interactions which hold the enzyme are affected, thus influencing the stability of the enzyme. A change in electrostatic interactions may result in the unfolding of the polypeptide chains which may be irreversible thus resulting in the denaturation of the enzyme. Also, a change in pH has an effect on the electrostatic interactions if the substrate is bound with the enzyme by virtue of these forces [133]. Even when the reaction is being carried out at neutral pH, the environment surrounding the active site of the enzyme may be extremely acidic or alkaline. As with all chemical reactions, the rate of reaction of enzyme catalysis increases with an increase in temperature. However, this holds true only for a narrow range of temperature. Within this optimum temperature range, the rate of catalysis by an enzyme increases with an increase in temperature and approximately doubles for a 10°C rise in temperature. Beyond the threshold values of this range, the rate of catalysis is affected adversely, eventually leading to a loss in catalytic activity. This can also be explained by the effect of temperature on the structure of the enzyme. At high temperatures, the intramolecular interactions which hold the enzyme together are overcome by the increased vibrational energy of the molecular chains. Thus the optimum temperature range for a successful enzyme application is then decided by the structural stability of the enzyme at a certain temperature.

Surfactants also have a major influence on the stability of an enzyme. Generally, non-ionic surfactants are compatible with the enzymes while anionic surfactants have least compatibility. However, every enzyme-surfactant combination gives different results so the compatibility should be checked in each case [133].

It becomes clear from the above discussion that the advantage of carrying out a reaction under milder conditions by using enzymes can only be realised by ensuring the preservation of its catalytic activity. Besides maintaining the enzyme activity during the application, it has to be preserved during enzyme storage before applications. The most important parameters to be checked in this regard are the storage temperature and pH. Although the appropriate values of these parameters differ for different enzymes, generally, the solid enzyme formulations are stored below 25°C. Some enzymes may require temperatures below 4°C. However, care should be taken in the case of liquid enzyme formulations to avoid freezing as this can denature the enzyme irreversibly. A liquid enzyme formulation consists of about 10 - 40% of sugars or related compounds to maintain stability. Sometimes, calcium salts or ammonium sulphate are also added for this purpose [133].

Enzymes have been classified into six major classes according to the reaction that they catalyse. However, in the research described in this thesis, two types of enzymes have been utilised as discussed in the following sections. One of these is a carboxylesterase which is a sub class of the hydrolases, and the other is an oxidase which belongs to the group referred to as oxidoreductases.

2.8.5 Laccase

Laccase (1.10.3.2) is an oxidoreductase. Oxidoreductases are enzymes which catalyse the transfer of hydrogen, oxygen or electrons from one substrate to another. Laccase may be referred to as a polyphenol oxidase and also as a blue copper oxidase. Oxidases are those oxidoreductases which catalyse the transfer of hydrogen to molecular oxygen. Laccase is one of the lignin-modifying enzymes (LME) produced extracellularly by white rot fungi. The other LMEs include lignin peroxidase and manganese peroxidase. These enzymes are highly oxidative in nature and have broad substrate specificity [135-138]. White-rot fungi are the major source of laccase, although, laccase is also produced by plants, some insects and bacteria [139].

Laccase generally exists as a dimeric or tetrameric protein and the molecular mass of a laccase monomer lies within the range 50 – 390 kDa. Laccase is composed of variable amounts (up to 45%) of carbohydrate depending on the source [138-141]. As discussed earlier, the enzyme may be a simple protein or a conjugated protein in which some other organic entity or a metal is attached to the protein moiety of the enzyme. In the case of laccase, this non-protein moiety is a carbohydrate which may be mannose, glucose, arabinose, galactose etc. The protein moiety of laccase consists of about 520 – 550 units of amino acids. Besides the carbohydrate, the non-protein component of laccase also has four copper atoms in a single polypeptide chain. These copper atoms are arranged at three different copper binding sites along the chain which are the actual active sites of the enzyme. These copper atoms accept one electron from oxidisable substances while molecular oxygen which acts as a co-substrate is reduced to water by accepting four electrons. The oxidisable substances which act as substrates for laccase are aryldiamines, polyphenols, polyamines, aminophenols and lignin. After the reduction, laccase can regenerate its catalytic activity by giving away electrons to molecular oxygen [133, 141].

Laccase can be used in purified form as an isolated enzyme or the parent white rot fungus can be utilised as a whole organism to produce laccase *in situ*. White-rot fungus

has been widely studied for the decolourization of dyes, for example in effluent treatment, and is in fact the most successful of all of the microorganisms studied for this purpose [138]. White-rot fungi (basidiomycetes) degrade lignin and other organopollutants. Although there role is to degrade lignin, it has been shown by experiments that it can also degrade man-made pollutants [142]. It has also been reported that *Phanerocaete chrysosporium* decolourises azo, anthraquinone, heterocyclic, triphenylmethane and polymeric dyes. The rate of dye decolourization and the mechanism of degradation may vary among different ligninolytic enzymes produced from the same organism [135, 143].

Laccases exhibit a range of redox potentials, from about +430 mV to +780 mV, depending upon its source with fungal laccases showing higher values [140, 144]. It has been used in the oxidation of azo and anthraquinone dyes. Sometimes, a chemical redox mediator such as ABTS (2,2´-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid)diammonium salt) or 1-hydroxybenzotriazole, which acts to provide an electron shuttle between the enzyme and the dye, is used to enhance the specificity of the laccase [78, 145]. It degrades the dye without breaking the azo double bond which precludes the formation of carcinogenic aromatic amine products [140, 146]. There are also some reports of oxidation of PET by laccase to improve its hydrophilicity [145, 147, 148]. However, these claims have attracted mixed opinions and some reports suggest that the increase in hydrophilicity by laccase is only due to the adsorption of the protein on the fibre surface [149].

2.8.6 Carboxylic Ester Hydrolases

Carboxylic ester hydrolases (3.1.1) belong to the hydrolase class of enzymes, which are the enzymes which catalyse the hydrolysis of C—C, C—N, C—O or other bonds [133]. As the name suggests, these are the enzymes which hydrolyse the ester bond. Depending upon the type of ester bond being hydrolysed, they may be further classified as, for example, lipases or triacylglycerolesterases (EC 3.1.1.3), which hydrolyse triacylglycerols and carboxylesterases (EC3.1.1.1) which hydrolyse carboxylic acid esters [150]. However, this classification is sometimes overlapping. For example cutinases (EC 3.1.1.74) hydrolyse triglycerides as well as primary alcohol esters[148]. In such cases, there are some other features which are used to distinguish the enzymes. For example, lipases have been shown to have interfacial activity. However, cutinase, which is a sub class of triacylglcerolesterase as it hydrolyses triglycerides, does not show any interfacial activity [133]. Thus, carboxylesterases or esterases act on water

soluble carboxylic acid ester molecules. Lipases show more specific activity towards aggregated molecules in water while cutinases hydrolyse both soluble and emulsified esters [151, 152].

The characteristic feature of lipases which distinguishes them from other esterases or enzymes showing lipolytic activity is their interfacial activation. This property is due to the presence of a so-called lid feature in its structure. The lid covers the active site and changes its conformation to expose the active site when the solvent conditions change. This way, the hydrophobic active site which is normally covered by the lid is then able to interact with the substrate molecules which are lipids [153, 154]. Lipases also need calcium ions for their hydrolytic activity. In contrast to lipases, cutinases have an open confirmation where the active site is always available to water and the active site can only bind to acyl structures [155, 156].

Cutinases belong to a group referred to as serine hydrolases and act specifically on primary alcohol esters. However, they have broad substrate specificity. Cutinases are quite stable enzymes and can withstand higher temperatures, up to about 70°C. Fungal cutinases are stable in an acidic medium down to pH 4 whereas bacterial cutinases can withstand alkaline medium up to pH 11 [148].

2.8.7 Applications

The catalytic function of enzymes has been exploited for industrial processes and new avenues are being explored constantly. The important characteristic of enzymes which has made them so desirable is that, unlike chemical catalysts, enzymes operate at ambient conditions involving a milder temperature and pH and that their action is substrate specific, that is, they will catalyse the reaction for a specific substrate only. On an environmental level, enzymes do not produce any undesirable by-products and are biodegradable [140, 157].

In textiles, enzymes have been used successfully for quite a long time. Among the textile applications, the most important and commercially successful is the desizing of cotton where the enzymes referred to as amylases hydrolyse the starch coating that has been applied on cotton. Other applications include stone washing of denim with laccases, removal of hydrogen peroxide after bleaching using catalases, wool finishing and degumming of silk with pectinases [133]. Other than that, research is ongoing for the use of enzymes in effluent treatment for decolourization purposes. Another area of interest for researchers is the modification of surface characteristics and thus surface

related properties, such as wettability, hydrophilicity and softness of the synthetic fibres including polyester and polyamide. The use of enzymes on polyester has yet to find wider commercial acceptance but research is under way on different levels.

Lipases and cutinases have been reported to increase the hydrophilicity of polyester by hydrolyzing the ester groups of the polyester. This enzymatic treatment is able to improve the wetting characteristics of polyester at lower treatment temperatures and with shorter times than alkaline hydrolysis. As discussed in Section 2.3.1, polyester is treated with alkali at high temperatures to improve the surface characteristics. Although hydrophilic properties are imparted, the mechanical strength is decreased. The action of the enzymes is limited to the surface of the polymer due to its molecular size and thus there is no loss of either strength or mass, as is the case with alkaline hydrolysis [158].

M Y Yoon et al. have investigated the hydrolysis of polyester by polyesterase. They have quoted an increase in hydrophilicity, easier removal of oily stains, lower pilling and a decrease in lustre. They have suggested that the polyesterase cleaves the ester groups in the polyester chain and results in the formation of solubilising hydroxyl and carboxylic acid end groups [159].

Cutinases have been widely studied for the hydrolysis and surface modification of PET. Although the temperatures generally reported for the stability of cutinase are about 25°C, there are some reports of improvement of the temperature stability to about 80°C [145, 149]. It has also been demonstrated that cutinases have higher activity for amorphous polyester as compared to crystalline polyester [145, 160, 161]. Cutinases have also been used for bio-polishing of polyester and blends of polyester with cotton [162]. Cutinases are also reported to hydrolyze the cyclic oligomers of polyester [163].

A comparison of cutinase and lipase in the hydrolysis of polyester fabric shows that both enzymes improve the hydrophilicity of the fabric. However, some differences can be observed in the behaviour of the two enzyme types. For example, on increasing the concentration of cutinase beyond the optimum range, the rate of the reaction decreased while in the case of lipase, it remained constant. Similarly, the hydrophilicity of polyester fabric increased when the cutinase was used with a surfactant [164]. However, in the presence of high concentration of surfactants, lipase activity is adversely affected because the surfactants change the surface characteristics of polyester from hydrophobic to hydrophilic, and lipases can effectively catalyse hydrophobic surfaces only [160]. Cutinases and lipases, in general, tend to adsorb on PET during

treatment which makes the assessment of surface properties of treated PET difficult [162, 165].

Esterases have been used in detergent formulation for the removal of oil based stains while some esterase have been reported to hydrolyse the ester bonds of polyester [133]. In a patent filed by Novozymes, esterases have been claimed to remove the surface deposits of disperse dye from the dyed fabrics thus replacing conventional reduction clearing. This method appears rational but the limitation is that it can be applied only for disperse dyes containing an ester group [166].

Despite the environmental benefits of using enzymes, there are certain other factors which have limited their widespread use in some areas. This is associated with the instability of enzymes, the cost of the isolation and purification of enzymes [140]. It should also be noted that enzymes do not produce toxic by-products but their presence in the effluent may increase the chemical and biochemical oxygen demand. However, enzymes are used at quite low concentrations as compared to treatments using chemical compounds in textile applications, and this issue can be managed by removing the enzyme proteins from the effluent before discharging. There are a number of techniques which can be used for this purpose such as precipitation and filtration [133, 162].

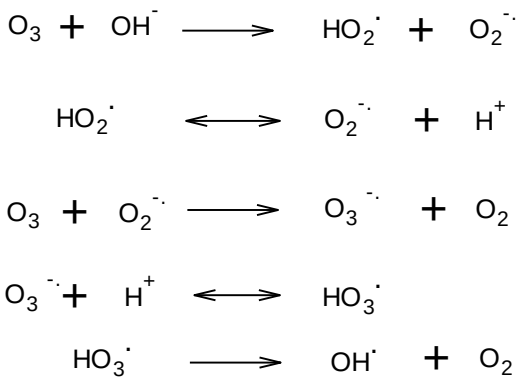
Another factor which hinders the successful application of enzymes in the textiles is the fabric structure and the enzyme molecular size. Most of the processes have been designed by trial and error rather than process engineering [133].

2.9 Oxidative Clearing

Although reduction clearing is the commonly used process for the removal of deposits of disperse dyes after dyeing, there are some instances where this process is unable to improve the fastness properties. As discussed in Section 0, the azo chromophore is cleaved irreversibly during reduction clearing while the anthraquinone disperse dyes are reduced and solubilised. There is a tendency for the reduced anthraquinone disperse dyes to be re-oxidized before their effective removal from the fabric. In such cases, an oxidative clearing may be preferred over reduction clearing. Sodium perborate or sodium hypochlorite may be used for oxidative clearing. However, an antichlor treatment after the use of sodium hypochlorite is required to remove the traces of chlorine [9, 17].

In some reports, hydrogen peroxide has been used to clear disperse dyed polyester and blends of polyester with cotton oxidatively. The redox potential of hydrogen peroxide is +1.77 V. According to the results provided by a study, this treatment produced higher wash fastness than conventional reduction clearing without producing a significant colour change. Oxidative clearing with hydrogen peroxide also led to a lower value of COD of the effluent [167]. In the case of polyester cotton blends, oxidative clearing is valuable when the dyeing is carried out in a neutral bath and dyed fabric cannot be subjected to conventional reduction clearing due to degradation of reactive dyes [168].

Another oxidizing agent which has lately been the focus of research in textiles is ozone. Ozone is an allotrope of oxygen; unlike oxygen, it is quite unstable and consequently, it acts as a strong oxidizing agent. It has an oxidation potential of +2.08 V in an acidic medium which decreases to +1.4V under alkaline conditions. Ozone is generated from oxygen by corona discharge and ultraviolet irradiation. The corona discharge process has been used for the production of high concentrations of ozone. Ozone is produced commercially by the application of a voltage across a discharge gap in the presence of oxygen. It is always produced *in situ* as it has a short life time of about 20 minutes in distilled water at room temperature.



Scheme 2.21 Decomposition of ozone

When dissolved in water, the stability of ozone depends upon the pH. It is stable under acidic conditions and unstable under alkaline conditions. As the pH increases, it decomposes into various free radicals such as $HO\cdot$, $HO_2\cdot$, $HO_3\cdot$ and $HO_4\cdot$ which are secondary oxidants (Scheme 2.21). Among these secondary oxidants, the $OH\cdot$ radical is the most important with an oxidation potential of +2.8V [169, 170].

Ozone has been used to decolourise disperse dyes in textile waste waters alone or in conjunction with other methods. To study the effect of ozone on dye decolourisation,

the waste water from a pilot textile dyeing plant was subjected to ozonation. It appears that aromatic rings are more reactive towards ozone than the azo bond. Dyes having olefinic and hydrazone groups react readily with ozone while metal-containing dyes and anthraquinone dyes are rather stable to it. The values of TOC and COD were reduced whereas BOD increased after ozonation treatment. This suggests that chemical substances underwent biodegradation after ozone treatment [171]. Ozone is very effective in removing the colour of water-soluble dyes but is less than satisfactory for water insoluble dyes such as vat and disperse dyes. It has been reported that disperse dyes, as a class, generally respond poorly to ozonation just as they do towards other decolourisation treatments. However, ozone treatment was not able to decrease the COD and TOC of the effluent as had already been observed in the case of other dye classes; thus ozone is not a recommended process for reducing the soluble organic content of the system [172-175]. Ozone generation is also quite expensive and the reactive species generated have a short life time [140].

In a study of disperse dyed polyester, ozone has been used for after clearing and simultaneous decolourization of dyebath effluent after disperse dyeing of polyester. The results indicate comparable washfastness results to that of sodium dithionite and a reduction in COD of the effluent [176].

In another related study, polyester fabric samples dyed with three blue disperse dyes having low, medium and high energy levels, were cleared with ozone and compared with conventional reduction clearing. Ozonation was carried out at room temperature and for varying time periods from 1 min to 15 min. The conventionally reduction cleared samples were set as the standard against which all the colour measurements were taken. According to the results of the study, when the ozonated samples were compared with the conventionally reduction cleared samples, there was not much difference in the lightness given by samples dyed with light and medium energy dyes. However, there was a significant change in lightness of the samples dyed with high energy blue dye. It is interesting to note that the high energy blue dye was the only azo dye among the three selected blue dyes. In contrast, the change in chroma was insignificant in the case of the samples dyed with high energy dyes and was highest for the samples dyed with medium energy dyes. The samples dyed with both low and medium energy dyes showed a lowering of chroma after ozonation. It is proposed that hydroxyl free radicals produced by the decomposition of ozone in neutral to slightly alkaline medium can penetrate inside the polymer and thus oxidise the disperse dye

present in the interior of the polymer. Thus, the study shows that ozonation improves the washfastness properties of the dyed samples, but that this is offset by the change in colour of the treated samples. Another limitation is that ozonation for longer than 1 minute produced a reduction in mechanical strength of the fabric [167]. In another study by Eren et al., the effect of ozonation on the removal of surface deposits of oligomers on polyester was reported. It was observed that ozonation removed oligomers to a similar extent as conventional reduction clearing [15].

Ozone has also been reported for the reduction clearing of disperse dyed PLA fabrics. In this method, ozonation serves two purposes. The first is the oxidative clearing and the other is the decolourisation of the dyeing effluent. However, the results indicated that to obtain satisfactory improvement in fastness properties a soaping step had to be included after ozonation because higher doses of ozone led to unacceptable colour differences. The positive aspect of this treatment is the reduction in chemical oxygen demand of the effluent when compared with traditional reduction clearing with sodium dithionite [177].

In another study concerning the clearing of disperse dyed polyester with ozone, a different technique was used. Instead of passing ozone through the liquor containing the fabric, ozone was blown directly onto wet fabric samples. The washfastness of the samples was improved to a comparable level to that provided by conventional reduction clearing and there was no significant loss in tensile strength. Thus, this technique appears to provide the advantage of lower water consumption [177].

Ozone has strong toxicity towards animals. The toxicity of ozone and the associated capital cost should also be considered when planning its use on a commercial scale. There has been a continuous debate on the possibility that by-products of oxidation of dyes may be toxic or even carcinogenic. In fact it has been proved that ozone reacts with the soluble degradation products of dyes resulting in the formation of species which are resistant to further oxidation [175, 178-180].

2.10 Plasma Treatment

Plasma is sometimes referred to as the fourth state of matter. It is composed of ions, radicals and atoms, either having different individual charges or neutral. However, plasma as a complex does not have any overall charge. This property is termed the quasi-neutrality of the plasma, that is, a state having equal numbers of positive and negative charges. Plasma can be generated by applying sufficient energy to a gas at low

pressure so that the gas is ionized. In fact, plasma is an ionized gas consisting of different species with the whole system at room temperature. When plasma comes into contact with a solid surface, a number of reactions take place, such as chain breaking and the formation of new functional groups. The uniqueness of the plasma treatment stems from a number of factors. These include its superficial action without affecting the properties of the bulk material and the fact that it is a cold, dry process. Plasma can induce some major effects on the surface of the substrate with which it is brought into contact. Some of these effects are etching, surface activation and deposition [181].

Plasma treatments have long been used successfully in the microelectronics industry. It has only been recently that their potential in the textile industry is being realized. There has been much work on the plasma treatment of natural fibres, notably wool [182-184]. Plasma treatment has been used to improve the hydrophilicity and dyeability as well as increasing the hydrophobicity of polyester [185-190].

Plasma techniques can be used to increase the colour intensity of dyed polyester. Techniques such as plasma polymerisation and sputter etching are helpful in this regard. Plasma polymerization involves the *in situ* polymerization of a polymer on the polyester surface [191]. Acrylamide functionality can be grafted on to a polyester surface through plasma to improve the hydrophilicity of polyester. Silyl containing groups have also been grafted onto the polyester surface to improve its hydrophilicity [189].

Plasma cleaning of polyesters fibres before metallization is also reported. Plasma cleaning has been carried out for removing the spin finishes from polyester fibres to prepare them for subsequent metallization [192]. The organic impurities are decomposed into CO_2, CO, H_2O and H_2 by plasma etching [193].

There has also been one brief report of research on the use of plasma for the clearing of disperse dyed polyester. It has been reported only for disperse dye padded onto the fabric surface rather than carried out using the traditional dyeing procedure. Oxygen, air, water vapour and hydrogen gas were used as the feeding gases. Washfastness was determined after the plasma treatment and hydrogen gas appeared to be the most effective according to the results obtained [194].

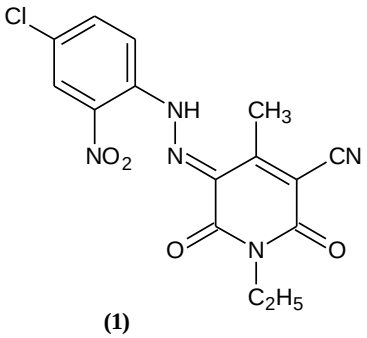
Chapter 3 - Experimental

3.1 Materials

The fabric used for the experiments described in this research was 100% polyester, with 57 ends cm^{-1} and 28 picks cm^{-1}. The count of the warp and weft was 18 and 37 tex respectively while the specific weight (weight of the fabric per unit area) of the fabric was 232 g m^{-2}. It was obtained from Toray Textiles Europe Ltd., Mansfield, UK. The fabric was prepared for processing quality and was used for dyeing without any pre-treatments. Five disperse dyes which represent the three basic colours and belong to different energy levels were used to dye the fabric. Duracet Yellow 4G (**1**), Duracet Red 3BL 150 % (**2**), Duracet Rubine GFL (**3**) and Duracet Brilliant Blue 8G 200 % (**5**) were supplied by Townend Plc Leeds, West Yorkshire, UK while Foron Blue S-BGL (**4**) was obtained from Clariant Distribution UK Ltd., Horsforth, Leeds, UK. The structures of the dyes are shown in Figure 3.1. Three of the selected disperse dyes contain the azo chromophore while the two blue dyes have anthraquinone chromophoric groups. Dye **4** is a mixture of two different anthraquinone dye structures. The ratio of the two structures is undisclosed for proprietary reasons.

The chemical reducing agents which were used in the research were sodium dithionite, formamidine sulphinic acid / thiourea dioxide (FAS/TUDO), hydroxyacetone, D-glucose and 9,10-anthraquinone-2-sulphonic acid sodium salt monohydrate. These were sourced from Alfa Aesar, Heysham, Lancashire, UK. Synperonic BD-100, a non-ionic detergent which was used during the clearing treatments, was obtained from Univar, Cheshire, UK. Two different types of enzymes were used as clearing agents. NS29076, an enzyme with lipolytic activity (a cutinase), was kindly provided by Novozymes A/S, Chinese Division while a laccase, from *Trametes versicolor*, an oxidoreductase, was acquired from Sigma Aldrich Company Ltd. Gillingham, Dorset, UK. NS29076 is an enzyme preparation while laccase is a purified enzyme. The activity of laccase was described by the suppliers to be 20,000 U g^{-1}. 1-Hydroxybenzotriazole hydrate was also acquired from Sigma Aldrich Company Ltd. UK.

SDC Multifibre DW fabric and ECE Phosphate Reference Detergent (B) for washfastness tests were purchased from SDC Enterprises Ltd., Bradford, UK. Grey scales for assessing change in colour and staining were also obtained from SDC Enterprises Ltd., Bradford, UK.



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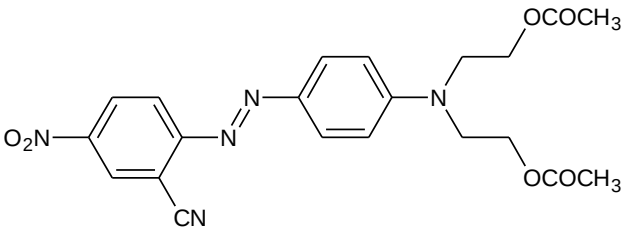

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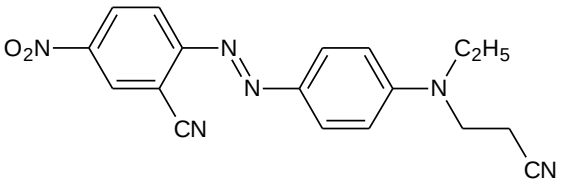

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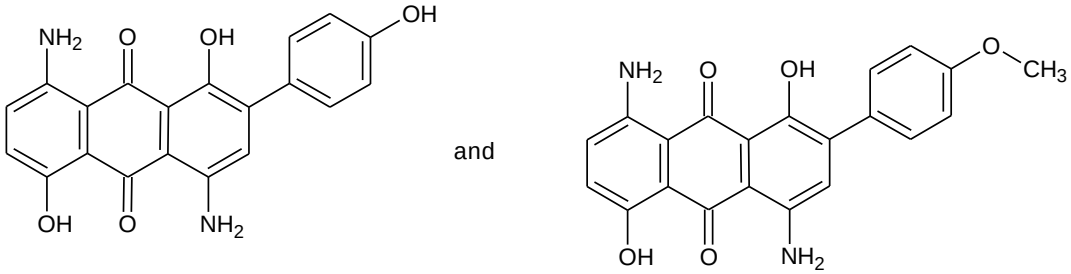

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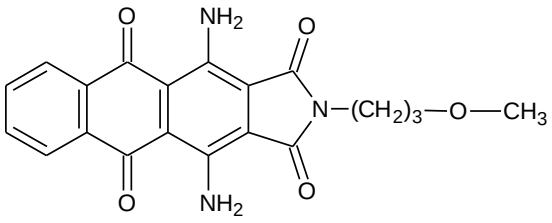


(5)

Figure 3.1 Dye structures, **1** - Duracet Yellow 4G, **2** - Duracet Rubine GFL, **3** - Duracet Red 3BL, **4** - Foron Blue S-BGL, **5** - Duracet Brilliant Blue 8G

Sodium perborate tetrahydrate was bought from Henkel kGaA, Hatfield, Herts, UK. All the other reagents used were standard laboratory grade and were sourced from Alfa Aesar, UK, if not stated otherwise.

3.2 Instrumental Equipment

All dyeing and clearing experiments were carried out on a Pyrotec-S IR dyeing machine manufactured by Roaches International, Birstall, West Yorkshire, UK, if not stated otherwise. Treatment with enzyme for time periods longer than 8 hours could not be performed on the Pyrotec-S as the automatic programmer could only accept time periods of a maximum of 8 hours. For this reason, treatment of fabric samples with enzymes for time periods longer than 8 hours were carried out on a Gyrowash from James Heal, Halifax, UK. Washfastness tests were also performed on the Gyrowash. The absorbance of the solutions was measured on a Perkin Elmer Lambda2 UV/Visible spectrophotometer while the colour measurements of the fabric samples were determined with a Datacolor Spectraflash SF600 reflectance spectrophotometer. A Hitachi S-4300 Scanning Electron Microscope was used for taking the images of the fabric samples. Fabric samples were sputter coated on a Polaron SC 7620 Sputter Coater before the scanning electron microscopy. The redox potential was measured with a pH Ion Redox meter from Eutech Instruments Europe B.V., The Netherlands. A Büchi Rotavapor-124 rotary evaporator was used for the evaporation of extracted dye solutions during the dye purification procedure. The cyclic voltammetry was performed using an Ecochemie Auto Lab, Pstat 10 system. The batch electrochemical reduction clearing experiments were carried out using an EG&G Princeton Applied Research Potentiostat/galvanostat Model 273. All the experiments with the exception of electrochemical experiments were performed in the dyeing and organic chemistry laboratory facilities of the School of Textiles and Design, Heriot Watt University. The electrochemical experiments were carried out in the Department of Pure and Applied Chemistry, The University of Strathclyde, Glasgow.

3.3 Methods

3.3.1 Dyeing

Five depths of shade, which are 1, 2, 3, 4 and 5% o.m.f., were used to dye the fabric. The quantity of dye used was calculated on the basis of the mass of the fabric. A 15 g fabric sample was used for all the dyeing experiments. All the dyeing experiments were carried out using a liquor ratio of 14:1. The total volume of the liquor, including all the chemicals was 210 ml. Disperse dye dispersions were prepared by dispersing the calculated amounts of dye, which were 0.15 g, 0.3 g, 0.45 g, 0.6 g and 0.75 g for the five depths, in de-ionized water. Acetic acid and ammonium acetate were used to adjust the pH so that it was in the range 4.5 to 5.5. Dye dispersions were made up to the

required volume, 210 ml for each dyeing, with deionised water. All the dyeings were carried out on the Pyrotec-S, IR dyeing machine (Roaches). Initially, the temperature was increased to 70°C at a rate of 3°C min^{-1} and then to 130°C at a rate of 1.5°C min^{-1}. Dyeing was continued for 30 minutes at 130°C and then the temperature was decreased at 1.5°C min^{-1} to 40°C. A schematic of the dyeing procedure is shown in Figure 3.2. All the dyed samples were rinsed twice in water at 90°C and once in water at 40°C. Drying of the samples was carried out at 50°C.

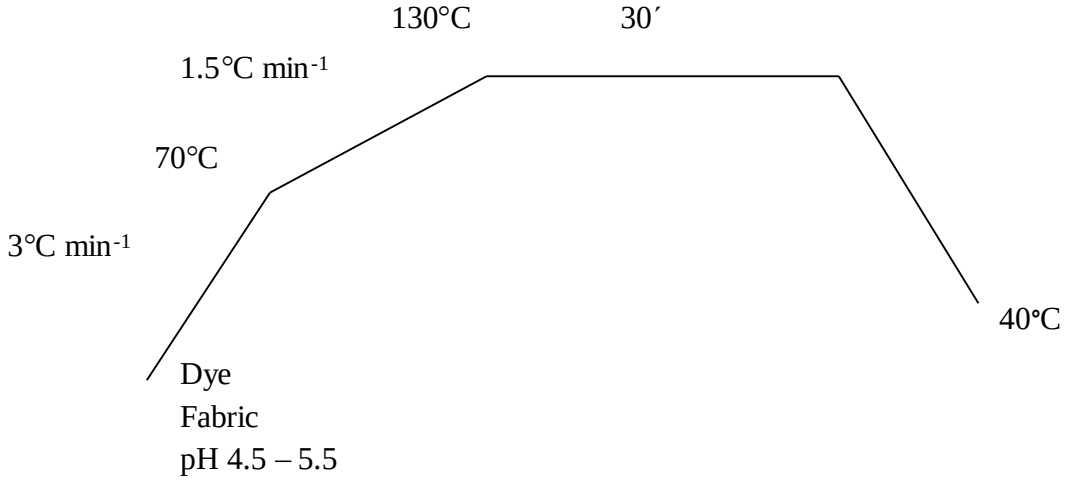


Figure 3.2 Procedure for dyeing of polyester with disperse dyes

3.3.2 Reduction Clearing

A 15 g fabric sample was used for all of the initial experiments. Afterwards, the optimization experiments were carried out with a 5 g sample of the dyed fabric. The dyed fabrics were reduction cleared with aqueous solutions containing 2.14 g l^{-1} sodium dithionite and 2.14 g l^{-1} sodium hydroxide in the presence of 1.07 g l^{-1} Synperonic BD-100, a non-ionic detergent, for 20 min at 70°C and a liquor ratio of 14:1. The fabrics were then rinsed twice in water at 90°C and once in water at 40°C. Finally, drying was carried out at 50°C. All the reduction clearing experiments were carried out using the Pyrotec-S IR dyeing machine.

3.3.3 Reduction Clearing with Organic Reducing Agents

Initially, reduction clearing of the dyed samples with formamidine sulphinic acid/thiourea dioxide (FAS/TUDO) and hydroxyacetone was carried out using an aqueous solution at a concentration of 2.14 g l^{-1} both of reducing agent and sodium hydroxide. In this set of experiments the concentration of the organic reducing agents and conditions were kept the same as were used for conventional reduction clearing

with sodium dithionite. Thus, reduction clearing was carried out for 20 min at 70°C in the presence of 1.07 g l^{-1} Synperonic BD-100 using a liquor ratio of 14:1. All of the dyed samples at all depths of shade were treated with these two organic reducing agents. Reduction cleared samples were rinsed and dried as described in Section 3.3.2 for conventional reduction clearing. Subsequently, reduction clearing of samples dyed with dye **3** at all depths of shade was performed using a concentration of 0.54 g $l^{-1}$for each of the two organic reducing agents. The time of treatment and concentration of surfactant was kept constant for all the experiments.

Table 3.1 Range of experiments used for optimisation of reduction clearing with glucose for samples dyed with dye **3** (3% o.m.f)

Concentration of glucose (g l^{-1})	60			30		10			5			2	
Concentration of alkali (g l^{-1})	2		8	2	8	20	8	8	8	4	4	4	2
Temperature (°C)	70	90	70	90	90	90	90	90	90	90	90	90	90
Time (min)	20	20	20	20	20	20	40	20	20	20	40	20	20

An optimization of parameters was carried out for experiments using glucose as a reducing agent. The optimization experiments were performed with samples dyed with dye **3** at 3% depth of shade only. The range of experiments used for reduction clearing with glucose is shown in Table 3.1. The first parameter to be optimised was temperature. Two different temperatures were used for this set of experiments; 70°C and 90°C. Conventional reduction clearing was carried out at 70°C, so this temperature was used for comparison purposes while a temperature of 90°C was used as it has been reported in literature that glucose is effective only at high temperatures [2, 9, 32, 89, 96]. A concentration of 60 g l^{-1} glucose was used to optimise the temperature. Alkali was used at concentrations of 2 g l^{-1} and 8 g l^{-1} for this first set of optimization experiments. In the next set of experiments, the temperature was kept constant at 90°C and the concentration of glucose was decreased to 30 g l^{-1} while alkali was used at the concentrations of 2 g l^{-1} and 8 g l^{-1}. In the third set of experiments, the concentration of glucose was reduced to 10 g l^{-1} while the time for reduction clearing was increased to 40 minutes for one experiment. Alkali was used at concentrations of 8 g l^{-1} and 20 g l^{-1}. In the fourth set of experiments, the concentration of glucose was decreased to 5 g l^{-1}. Alkali was used at concentrations of 4 g l^{-1} and 8 g l^{-1} while the temperature for the

treatment was varied as 20 and 40 minutes. Finally, 2 g l^{-1} glucose was used at an alkali concentration of 2 g l^{-1} and 4 g l^{-1} at 90°C for 20 min. The concentration of the non-ionic surfactant was kept constant at 1 g l^{-1} for all the experiments. All the treated samples were rinsed twice in water at 90°C and once in water at 40°C. The optimized conditions which were 2 g l^{-1} glucose, 2 g l^{-1} sodium hydroxide at 90°C for 20 min, were then used for the reduction clearing of the rest of the dyed samples, that is, samples dyed with dyes **1**, **2**, **4** and **5** at 3% depth of shade.

3.3.4 Detergent-based Wash-off

The dyed fabrics were subjected to a detergent-based wash-off procedure according to a previous publication [18]. Fabric samples were treated with aqueous solutions containing 4 g l^{-1} ECE detergent, 1 g l^{-1} Na_2CO_3 and 1 g l^{-1} sodium perborate at 98°C for 15 min in Pyrotec-S, IR dyeing machine. A liquor ratio of 20:1 was used. The fabrics were rinsed in warm water and cold running water respectively. Fabrics were then dried at room temperature.

3.3.5 Clearing with Enzymes

(a) Molar extinction coefficient of *p*-nitrophenol (PNP)

p-Nitrophenol (5 mg) was weighed accurately on an analytical balance. An aqueous potassium phosphate buffer (50 mM) at pH 7.5 was prepared according to the Sigma test method [195]. The *p*-nitrophenol was then dissolved in a little buffer in a 100 ml flask and the volume made up to 100 ml with buffer. The absorbance of this solution was measured on a Perkin Elmer Lambda2 UV/Vis spectrophotometer at 420 nm against the buffer solution as control. The extinction coefficient of *p*-nitrophenol was calculated using the Beer Lambert equation. The absorbance was determined as 3.1 at 420 nm and the molar extinction coefficient was calculated to be 8.66 mmol l^{-1}.

(a) Measurement of enzyme activity

The activity of enzyme NS29076 was measured according to the standard method provided by Sigma Quality Control [195]. A 50 mM potassium phosphate buffer was prepared as outlined in the test method. 100 mM of *p*-nitrophenyl butyrate (PNPB) was used as a substrate for the enzyme instead of the *o*-nitrophenyl butyrate. The *p*-isomer was used because the *o*-isomer was not available commercially. 10 µl enzyme preparation, that is, NS29076 was pipetted out using a micropipette and the volume made up to 1 ml with deionised water. The volume of the enzyme preparation to be used was based on a number of trials carried out earlier. 2.87 ml of buffer solution and

0.03 ml of PNPB were added into two quartz cuvettes and loaded into the spectrophotometer in appropriate holders. The absorbance was measured on the spectrophotometer at 420 nm over 5 min and the result was noted as a blank. The cuvette in the test holder was removed and 0.1 ml of enzyme solution was added. The cuvette was inverted to mix the two solutions and quickly loaded back into the holder. The absorbance was measured at 420 nm over 12 min and the readings were noted as the test. Activity of the enzyme preparation was calculated according to the formula given in the test method.

The activity of laccase from *Trametes versicolor* was provided by Sigma Aldrich.

(b) Clearing With Esterases

Clearing with NS29076 was carried out at pH 8 on the basis of recommendations by the manufacturer, Novozymes. Initially, experiments were carried out in the presence of sodium citrate buffer. Buffer was also used to make a 1% stock solution of enzyme. However, sodium citrate did not provide the required buffering action and the results of the duplicate trials were not correlating. Thus, a change was made to phosphate buffer due to instability of the stock solution and poor reproducibility of the results. The range of experiments for the optimisation of conditions for clearing of dyed samples with NS29076 is shown in Table 3.2.

Table 3.2 Range of experiments for optimisation of clearing of samples dyed with dye **3** (3% o.m.f.) with NS29076

Time (hr)	0.5	1	2	4	5	6	16	20	24	2	2		2		2	2	
Temp (°C)	40									40	50	60	60		70	60	
pH	8									8	8		5	9	5	5	
Conc. (ml l^{-1})	1									2	1		1		1	5	10

First of all, time was optimised; time periods of 0.5, 1, 2, 4, 5, 6, 16, 20 and 24 were used while the temperature and pH were maintained at 40°C and 8 respectively. The concentration of enzyme for the first trial was taken as 1 ml l^{-1}. The results indicated that a time period of 2 hour gave optimum results and thus further trials were carried out for a time period of 2 hours. In the next set of experiments, temperatures of 40, 50 and 60°C were used while the pH was maintained at 8 with phosphate buffer. Concentrations of 1 ml l^{-1} and 2 ml l^{-1} NS29076 were used. As a result of this set of trials, a temperature of 60°C proved to be the optimum among the three selected values.

The third set of experiments was carried out to optimise the pH of the treatment. pH values of 5 and 9 were selected for the tests and the results showed that acidic pH was more suitable. Thus, the optimum values of the temperature and concentration proved to be 60°C and 1 ml l^{-1}. Finally, a higher temperature of 70°C was also used under acidic conditions. All of the optimisation experiments were performed with samples dyed with dye **3** at 3% depth of shade only. However, samples dyed with dye **2** at 3% depth were optimised for pH also because of the susceptibility of this dye to hydrolysis. The rest of the dyed samples were then cleared with NS29076 using the optimised conditions which were, 1 ml l^{-1} enzyme at pH 5 and 60°C for 2 hours. In addition, experiments were also carried out at 70°C, pH 5 for 2 hours with an enzyme concentration of 1 ml l^{-1} for all the other samples.

A blank control test without the addition of enzyme was carried out with all the experiments. The experiments for time periods greater than 8 hours were carried out on the Gyrowash in duplicate while the rest of the experiments were performed on the Pyrotec-S in triplicate. Afterwards, samples were rinsed twice in water at 90°C and once in water at 40°C while drying was carried out at 50°C.

(c) Clearing With Laccase From *Trametes versicolor*

Clearing with laccase was carried out on the Gyrowash for experiments with times longer than 8 hours and experiments with time periods 8 hours or less were carried out on the Pyrotec-S IR dyeing machine. The first experiment which was for a time period of 24 hours was carried out with and without 1-hydroxybenzotriazole hydrate (HBT). Afterwards all the experiments were performed in the presence of 1-hydroxybenzotriazole which acts as an activator/mediator. A 10 mM stock solution of 1-hydroxybenzotriazole was prepared and then used in the trials. Phosphate buffer was prepared with potassium dihydrogen phosphate and potassium hydroxide. It was used for the experiments at pH 5 and 7 while a citrate-phosphate buffer was used for experiments at pH 3. Citrate-phosphate buffer was prepared with 0.1 M citric acid and 0.2 M dibasic sodium phosphate. The enzyme was used as a 0.1% solution in buffer. The fabric mass was 5 g for all the optimization experiments and a liquor ratio of 14:1 was used. The first trial was carried out for 24 hours at pH 5 and 30°C using an enzyme concentration of 1000 U l^{-1}, as a set of three experiments, one as blank, another as enzyme without mediator and the third as enzyme with mediator. The results showed that mediator was quite effective in improving the performance, thus all the subsequent trials with laccase were carried out in the presence of mediator.

Table 3.3 Range of experiments for clearing of samples dyed with dye **3** (3% o.m.f.) with laccase from *Trametes Versicolor*

Time (hrs)	1	2										4	7	8	14	18	20	24		28	40	48
Conc. of mediator (mM l^{-1})	1	0.5	1						2	5		1	1	1	1	1	1	0	1	1	1	1
Temp. (°C)	30	30	25	30	40				50	30	30	30	30	30	30	30	30	30		30		
pH	5	5	5	5	3	5			7	5	5	5	5	5	5	5	5	5		5		
Conc. of Enzyme (10^{3} U l^{-1})	1	1	1		1	0.5	1	1.5	2	1	1	1	1					1		1		

In the second set of experiments, the time period was optimised. The range of experiments for optimisation is shown in Table 3.3. The following set of experiments consisted of trials which were carried out using various concentrations of mediator, 1-hydroxybenzotriazole. The results indicated that the optimum concentration of 1-hydroxybenzotriazole is 1 mM. After that, experiments were carried out by varying the temperature while keeping all other parameters constant. In the next set of experiments, pH was optimised using three different values. Finally, the concentration of enzyme was optimised. These optimisation experiments were carried out for samples dyed with dye **3** at 3% depth of shade only. The optimised conditions, which were 1000 U l^{-1} laccase, pH 5 at a temperature of 40°C for 2 hours in the presence of 1 mM 1-hydroxybenzotriazole, were then used for the clearing of all the other dyed samples. As with the clearing with esterases, all of the experiments with laccase were performed in triplicate and with control experiments which were carried out without the enzyme and mediator. In the laccase clearing, an additional control for the mediator was also carried out with the experiments. The solution of control for mediator consisted of buffer with mediator but no enzyme. Rinsing was carried out twice in water at 90°C and once in water at 40°C while samples were dried at 50°C.

3.3.6 Reduction Clearing with Iron Salts

Reduction clearing of the dyed samples with iron salts was carried out as a preliminary set of experiments prior to the electrochemical reduction clearing investigation. Samples dyed with dye **3** at a depth of shade of 3% were used for these preliminary trials. Iron (II) sulphate heptahydrate was used in the presence of sodium hydroxide and sodium D-gluconate (DGL) which acts as a complexing agent. The concentration of the three compounds, iron (II) sulphate, sodium hydroxide and sodium D-gluconate was varied in the ratios, 1:0:0, 1:0:1, 1:1:1, 1:2:0, 1:2:1, 1:2:2 for experiments carried out at 25°C. At a higher temperature of 60°C, concentrations were used in the ratio, 1:0:0, 0:0:2, 1:0:2, 0:2:1 for iron (II) sulphate, sodium hydroxide and DGL respectively. The concentration of iron (II) sulphate heptahydrate was kept constant at 0.01 M. The concentrations of alkali and sodium D-gluconate were varied with reference to the concentration of iron (II) sulphate. Stock solutions were prepared at concentrations of 0.05 M iron (II) sulphate heptahydrate, 0.05 M sodium D-gluconate and 0.1 M sodium hydroxide. The calculated amount of iron (II) sulphate was dissolved in a little deionised water. Sodium D-gluconate was then added and after its dissolution, sodium hydroxide was added and the solution made up to the required volume which was 70 ml

for a 5 g fabric sample. In some cases, it took about half an hour for complete preparation of the solution. Afterwards, the samples were rinsed twice in water at 90°C and once in water at 40°C. Treated samples were then dried at 50°C.

3.3.7 Electrochemical Reduction Clearing

Iron (III) chloride and 9,10-anthraquinone-2-sulphonic acid sodium salt (AQS) were selected as mediators for electrochemical reduction clearing. Triethanolamine (TEA) and sodium D-gluconate (DGL) were used as complexing agents for iron (III) chloride.

(a) Cyclic Voltammetry experiments

Cyclic voltammograms (CV) of iron (III) chloride-triethanolamine, iron (III) chloride-sodium D-gluconate and 9,10-anthraquinone-2-sulphonic acid sodium salt (AQS) were obtained before the reduction clearing experiments were carried out to determine the redox potentials of the mediators. The solutions were prepared according to the concentrations given in Table 3.4.

Table 3.4 Concentration of solutions used for electrochemical reduction clearing

Solution	$FeCl_3$	TEA	Na-DGL	AQS	KOH
1	0.0078 M	0.038 M	-	-	0.15 M
2	0.01 M	-	0.02 M	-	0.2 M
3	-	-	-	1 mM	0.1 M
4	0.007 M	-	-	-	pH 5.0
5	0.07 M	0.5 M	-	-	0.5 M

The weighed quantity of mediator was dissolved in deionised water, complexing agent was added and stirring was continued until the precipitate dissolved. Finally the weighed quantity of alkali was added and the volume made up to 100 ml with deionised water. Cyclic voltammetry experiments were carried out using a three-electrode cell configuration with an Ecochemie Auto Lab, Pstat 10 system. A glassy carbon electrode with a disk diameter of 7 mm, surface area 0.38 cm^2, was used as the working electrode while a platinum gauze was used as counter electrode. The reference electrode for all the electrochemical experiments was saturated calomel (SCE) which has a redox potential of + 0.242 *vs* SHE (standard hydrogen electrode). All of the solutions were degassed by bubbling nitrogen for the elimination of interference from atmospheric

oxygen before running the CV. The glassy carbon electrode was cleaned and polished before running a new sample. The cyclic voltammograms were obtained for the control solution, that is, mediator only, as well as after the addition of 0.1 g l^{-1} dye **3**. CV of dye **3** at a concentration of 0.1 g l^{-1} in phosphate buffer (0.066 M disodium hydrogen phosphate) was also carried out for comparison purposes.

(b) Reduction clearing experiments

The batch electrolysis experiments for the reduction clearing of dyed samples were carried out in a divided cell having a catholyte volume of 250 ml with a nafion membrane using EG&G Princeton Applied Research Potentiostat/galvanostat Model 273. A carbon fabric electrode (area 36 cm^2, immersed area 28 cm^2) was used as the working electrode and platinum coated titanium was used as the counter electrode for the batch electrolysis experiments. Samples of polyester fabric weighing 4 g, dyed with dye **3** at a shade depth of 3% were used for electrochemical reduction clearing experiments. A 0.1 M solution of KOH was used as anolyte and solutions 1, 2, 3 (Table 3.4) containing the fabric samples were used as catholyte. All of the experiments were carried out at room temperature. Batch electrolysis was performed under a nitrogen atmosphere. In the case of solution 5, the anolyte and catholyte were the same solution. In the first set of experiments, 500 ml of each of solutions 1, 2 and 3 were prepared. 200 ml of that solution were poured into the cathodic half cell. A similar volume of anolyte KOH (200 ml) was added to the anodic half cell. Fabric was placed in the cathode half cell, and the cell was set up for the experiment. The treatment was then carried out for 20 minutes at the specified potential. The potential was controlled at −1.1 V for solution 1 and −0.70 V for solutions 2 and 3. In the next set of experiments, fabric was treated electrochemically with solution 1 for 90 minutes at room temperature and with solution 3 for 60 min at room temperature. The potential was set at −1.2 V in both cases. Fabric was also treated with a 0.07 M solution of iron (III) chloride for 40 minutes at a potential of −1.2 V with the pH adjusted to 5 using acetic acid and sodium acetate. Solutions 2 and 3 were also used to treat the fabric without the electrochemical set up on the Pyrotec-S dyeing machine. In the next set of experiments, experiments were carried out at controlled current, that is, instead of setting up a potential value, current was set at a specified value. For this set of experiments, solution 5 was used as the catholyte. Experiments were carried out at current values of 0.25 A and 0.5 A. An experiment was also carried out to check the redox potential of the bulk solution with an external redox meter. The fabric was treated with solution 5 in this experiment for 40

minutes and 20 minutes at 0.25 A and 0.5 A respectively. After the electrochemical treatment, fabric was rinsed as described in the previous sections and dried at 50°C.

3.3.8 Assessment of the Clearing Effect

Since all the five dyes used in this study were commercial preparations, samples were purified for the measurement of extinction coefficients. All the dyes were purified by extraction with toluene in a Soxhlet apparatus for about 4 - 6 hours. However, dye **4** was extracted for a longer time of around 12 hours. The dye solutions obtained in toluene were evaporated using a Büchi Rotavapor-124 rotary evaporator to about one third of the original volume. The solutions were then kept in the refrigerator overnight for crystallisation. The solutions were subjected to vacuum filtration and the dye residues obtained were dried in oven at 60°C for 24 hours. 5 mg of purified dye was weighed out accurately on an analytical balance, dissolved in 100 ml acetone and the solution was diluted 10 times or 5 times depending upon the absorbance values obtained. The absorbance of the dye solutions was measured on a Perkin Elmer UV/VIS Spectrophotometer Lambda2 at the λ_{max} value. The gram extinction coefficients of each dye were calculated by using the Beer Lambert equation.

(a) Measurement of Surface Dye Removal

Assessment of the dye remaining on the fibre surface was carried out by immersing the sample in acetone under controlled conditions. A 1.0 g sample of dyed fabric was immersed in 10 ml acetone at 20°C for 10 minutes [196]. The fabric samples were taken out and the absorbance of the solutions was measured on a Perkin Elmer UV/VIS Spectrophotometer Lambda2 at the λ_{max} of each dye. The instrument was calibrated using pure acetone as a control before the measurements. All of the measurements were taken against the absorbance of acetone used as standard. Extracts with an absorbance of greater than 2 were diluted to provide absorbance values below 2.

(b) Determination of Fastness properties

Washfastness, rubfastness and fastness to acidic and alkaline perspiration of the dyed and treated samples were determined according to the test methods BS EN ISO 105-C06:C2S:1990 [197], BS EN ISO 105-X12:2002 [198], and BS EN ISO 105-E04:2009 [197] respectively. The multifibre fabric DW used as adjacent fabric in the washfastness testing is composed of six fibres, which are wool, acrylic, polyester, nylon, cotton and acetate, in that order. The test fabric (10 cm x 4 cm) was sewed with the same size of multifibre fabric, with the face of the test fabric in contact with the

multifibre fabric, along one of the short edges. The washfastness test was carried out at 60°C for 30 minutes in the presence of 25 steel balls to mimic mechanical action. The test samples for measuring the colour fastness to rubbing were mounted on the base of the testing device with the long direction diagonal to warp and weft. The white rubbing cloth for wet rubbing was soaked in distilled water just before the test to provide an uptake of 90 – 100%. Samples for fastness to perspiration were prepared in a similar manner to the samples for washfastness tests. The prepared composite samples with multifibre fabric were immersed in the freshly prepared acidic and alkaline histidine solutions for 30 minutes. The samples were then mounted on two perspirometers, one for acidic and the other for alkaline conditions which were then kept in an oven at 37°C for 4 hours. The change in colour and the staining of the adjacent multifibre fabric was graded against the ISO grey scale for colour change and staining respectively according to BS EN20105-A02:1990 and BS EN20105-A03:1990 [197].

(c) Colour Measurements

The colour coordinates, L*, a*, b*, C*, h°, of the original and treated samples were measured using a Datacolor Spectraflash SF600 under illuminant D 65 and 10° observer with the UV component and specular included. The instrument was calibrated by using a black trap, white tile and green tile respectively according to the manufacturer's recommendations with the LAV (large area view) aperture. Dyed fabric samples which were not subjected to any treatment were used as standards against which the reduction cleared sample was measured for each depth of shade of the five dyes. Samples were folded four times and measurements were made on the back of the fabric. Three measurements were taken at different parts of the sample and their average was used.

(d) Scanning Electron Microscopy

Images of dyed and treated samples were taken by a Hitachi S-4300, Scanning Electron Microscope at various magnifications. The samples were prepared with their back face on the top for the examination and were coated with gold palladium using argon as medium in a Polaron SC 7620 Sputter Coater before subjecting to microscopy. The coating process was carried out to prevent charge build up.

3.3.9 Assessment of the Environmental Impact of the Clearing Agents

The samples of the residual liquors after the clearing treatments were sent to Scottish Water, Edinburgh, for the measurement of biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Samples dyed with dye **3** at a concentration of 3% o.m.f. were treated with the clearing agents whose BOD was to be determined and the residual liquors were collected in the BOD bottles provided by Scottish Water. BOD/COD tests were carried out within 24 hours of collecting the residual liquors and samples were stored between 0 - 4°C before the testing at Scottish Water laboratory in Riccarton, Edinburgh.

3.3.10 Determination of the Redox Potential

The redox potential of the clearing agents was determined using a pH Ion Redox meter from Eutech Instruments with a Platinum pin electrode. The instrument was calibrated with an aqueous alkaline solution of sodium dithionite at concentrations of 5 g l^{-1} sodium dithionite and 10 ml l^{-1} of sodium hydroxide (38°Be) at 50°C to a redox potential of -850 mV. The test solutions were prepared with the same concentrations and conditions which were used for the clearing treatments. However, temperature could not be increased to 90°C, which was strictly required in the case of glucose, because of the limited temperature sensitivity of the electrode.

Chapter 4 - Results & Discussion

4.1 Introduction – Overview of Methodology

In spite of the widespread inclusion of the reduction clearing process in the dyeing and printing routines for polyester and its blends, little information from detailed experimental investigation could be found concerning the outcome and mechanism of the process in the scientific literature. Therefore, a first set of experiments was carried out to establish the importance of conventional reduction clearing and to validate its effect on the fastness and colouristic properties of the dyed polyester.

A comparison of various reducing agents for reduction clearing of polyester dyed with a black disperse dye has been made in a study by S. Anders as discussed in Section 2.5.3 [11]. Formamidine sulphinic acid/thiourea dioxide (FAS/TUDO) and hydroxyacetone have been explored as alternatives to sodium dithionite for reduction clearing of polyester dyeings and prints. An iron salt-gluconic acid complex was also reported for reduction clearing in this comparative study. However, only FAS/TUDO was reported to give results comparable to sodium dithionite. There are some reports of the use of iron salts in vat dyeing while glucose has been used successfully as a reducing agent for sulphur dyeing [89, 199, 200]. Specific anthraquinone compounds have been employed as catalysts during certain reduction processes [74]. However, most of the previous research was with dyes of unknown structure. It was understood that various types of dyes may respond differently to reduction clearing. Thus, in the research described in this thesis, it was planned to use alternatives that have been previously investigated, such as FAS/TUDO, hydroxyacetone, the detergent-wash and iron salt complexes, as well as compounds which have not been employed for reduction clearing before, such as glucose for the reduction clearing of the five selected disperse dyes with known chemical structures.

Reduction clearing with FAS/TUDO and hydroxyacetone was carried out to provide a comparison with sodium dithionite, and thus, optimisation experiments were not performed for these two organic reducing agents. Optimisation experiments were carried out in the case of clearing with glucose, iron salts and using enzymes. Dye **3** was selected for the optimization experiments as its fastness properties are only moderate and the change in colour is more discernible than with the blue and yellow dyes. It is noted that, dye **2** has a similar structure to dye **3**, although it has ester groups on the side chain which may be capable of hydrolysis by alkali which needs to be taken

into account in the assessment of the clearing effect. The general methodology for those optimisation experiments that were carried out was to optimise the conditions and concentrations with a selected dye (dye **3** at 3% o.m.f.). After the determination of the optimised conditions, the experiments were carried out at the optimised conditions for the rest of the dyed samples. A single depth of shade, which is 3%, was selected out of the five depths of shade for these experiments.

Two approaches were considered in the selection of enzymes which might offer the potential to effect clearing; firstly, hydrolysis of the superficial layer of polyester and secondly degradation of surface dye. Two types of enzymes were thus selected, one potentially capable of acting on the polyester surface and the other having redox properties. As an example of the first type, NS29076, a cutinase with lipolytic activity which has the potential to hydrolyse the ester groups in polyester was selected while the second type, laccase, an oxidoreductase which may have the potential to oxidise the dye molecules was selected.

Since fastness to perspiration, acidic and alkaline were in line with washfastness of samples reduction cleared with sodium dithionite, the former was excluded from the range of tests performed for the assessment of clearing efficiency in subsequent studies. As the mechanism of reduction involves gain of electrons, this feature can be achieved in principle by electric current flow. In a different textile dyeing context, electrochemical techniques have been used successfully to reduce vat and sulphur dyes, which is an essential part of their application process [201-203]. Both direct and indirect electrochemical techniques have been employed for the reduction of vat and sulphur dyes. Direct electrochemical reduction involves the reduction of dye particles as a result of direct contact with the cathode surface. In the indirect electrochemical process, the dye does not have to be in contact with the cathode itself. Instead, electron carriers which are referred to as redox mediators are used. These mediator compounds are reduced at the surface of the cathode as a result of gaining electrons. The mediator then travels away from the cathode surface into the solution towards dye particles and transfers these electrons to the dye molecule, which is thus reduced. The mediator is consequently oxidised in the process and then travels to the cathode surface where it can be reduced once again. Thus, the cycle continues until all the dye is reduced.

Since in the research described in this thesis, the aim is to remove dye that is on the surface of the fabric, indirect electrochemical reduction can be envisaged for reduction

clearing. Three different compounds, iron-triethanolamine, iron-gluconate and anthraquinone compounds have been employed as redox mediators in this work. Cyclic voltammetry is a useful technique to characterise the electrochemical properties of a compound. Thus, three selected mediators were characterised by cyclic voltammetry before the electrochemical reduction clearing. Batch experiments for electrochemical reduction clearing were carried out using two different methods, controlled potential and controlled current as described in Section 3.3.7. After electrochemical reduction clearing, fabric samples were assessed for possibility of improvement in their properties by carrying out acetone extraction and washfastness tests.

The redox potential of all the clearing agents was measured to study the relationship between their clearing efficiency and redox potential. The effect of the various clearing agents employed in the research on the effluent was also assessed by the determination of COD and BOD values of the residual treatment liquors.

4.2 Selection of Dyes

The dyes were selected on the basis of their energy level, fastness properties and availability. The commercial and CI generic names of the dyes with the numbering used in this thesis are shown in Table 4.1.

Table 4.1 CI and commercial names of the dyes and their classification

Dye	CI Name	Commercial Name	Chemical Class	Energy
1	Disperse Yellow 211	Duracet Yellow 4G	Azo	Medium
2	Disperse Red 82	Duracet Red 3BL	Azo	High
3	Disperse Red 73	Duracet Rubine GFL	Azo	Medium
4	Disperse Blue 73	Foron Blue S-BGL	AQ	Medium
5	Disperse Blue 60	Duracet Brilliant Blue 8G	AQ	High

Duracet Yellow 4G (**1**), Duracet Rubine GFL (**3**) and Foron Blue S-BGL (**4**) are medium energy level dyes while Duracet Red 3BL (**2**) and Duracet Brilliant Blue 8G (**5**) belong to the high energy class. High energy dyes have relatively higher molecular mass and are preferred for application by thermofixation. Both medium and high energy dyes can be used for high temperature dyeing methods while low energy dyes require a lower dyeing temperature for their application. Thus, low energy dyes are not used in this study to avoid variation due to dyeing methods. Dye **4** is described by manufacturers as a dye with high sublimation fastness and migration power. It is

mostly used for yarn dyeing and thermofixation methods but can also be used for exhaust dyeing.

The chemical structures of the selected dyes are shown in Figure 4.1.

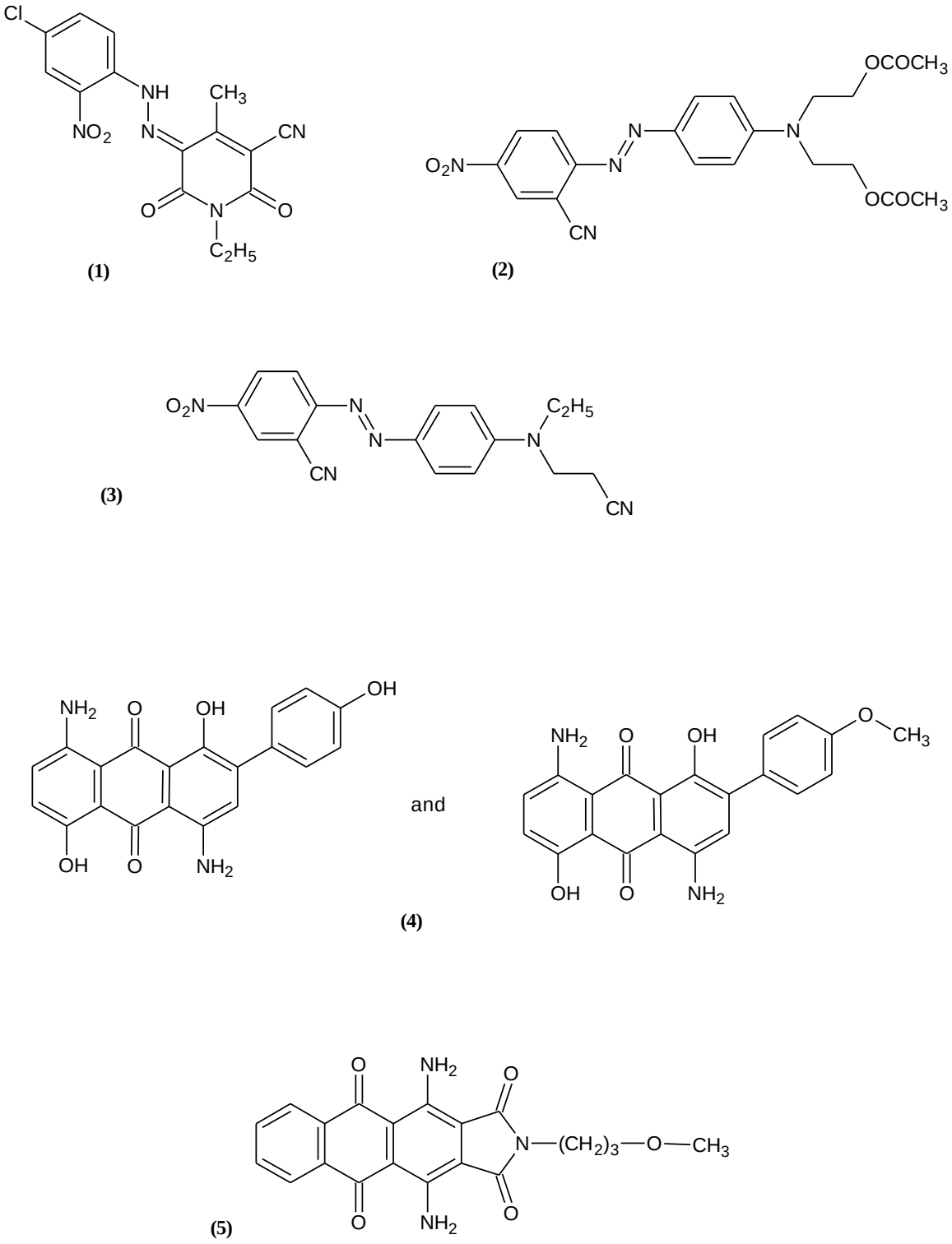


Figure 4.1 Chemical structures of the dyes

Dyes **1**, **2** and **3** belong to the monoazo structural group whereas dyes **4** and **5** have an anthraquinone (AQ) structure. Dyes **2** and **3** are structurally very similar with the only difference being the presence of methyl ester groups in dye **2** compared with ethyl and cyano groups in dye **3**. However, dye **2** is described as a high energy dye and dye **3** as a medium energy dye by the suppliers. This categorisation seems strange at first sight but it is understood that the classification of the dyes according to their energy levels can be described as arbitrary to a certain extent with much overlap among different classes.

4.3 Selection of Substrate

100% Polyester fabric was used for the experiments; it is a heavy quality twill fabric with a specific face and back. The fabric was used without subjecting to any preparation, as it was obtained in a "prepared for print" form.

4.4 Reduction Clearing with Sodium Dithionite

Polyester (polyethyleneterephthalate, PET) is dyed virtually exclusively with disperse dyes. Because of the limited water-solubility of disperse dyes and a tendency for particles in the dispersion to aggregate during the dyeing process, some residual dye commonly remains on the fibre surface at the end of the dyeing phase. These surface deposits may have an adverse effect on the colouristic and fastness properties of the dyed fabrics and thus an aftertreatment to remove them is commonly introduced. The process that is conventionally used, referred to as reduction clearing, involves treatment of the dyed polyester with an aqueous alkaline solution of a reducing agent at temperatures below the boiling point of water. Sodium dithionite is the reducing agent traditionally used for the reduction clearing of polyester dyeings and prints. In spite of the widespread inclusion of the reduction clearing process in the dyeing and printing routines for polyester and its blends, little information from systematic investigations could be found about the process in the scientific literature. Therefore, the first set of experiments was carried out to establish the importance of conventional reduction clearing and to validate its effect on the fastness and colouristic properties of the dyed polyester. Polyester fabric was dyed with a series of five selected disperse dyes of known structures at concentrations of 1, 2, 3, 4 and 5% (o.m.f.). This selection was made so that the commercially important depths of shade are included and also because reduction clearing is generally accepted to be more important for higher depths of shade [10]. The dyeing procedure used was devised according to the recommendations of the dye manufacturer and is described in detail in Section 3.3.1. Dyeing was carried out at 130°C for 30 minutes as this combination of time and temperature was judged to be

appropriate to ensure a balance between minimising the time while achieving sufficient dye exhaustion. The temperature gradient was initially 3°C min^{-1} and was then decreased to 1.5°C min^{-1} after reaching 70°C, which is below the beginning of the glass transition temperature range of polyester, to provide level dyeing. All of the fabrics dyed with the selected disperse dyes at all five depths of shade were reduction cleared with sodium dithionite using a standard recipe as outlined in the Section 3.3.2. Detergent was included during reduction clearing to avoid the redeposition of suspended dye particles on the fabric surface. The effect of reduction clearing on washfastness, rubfastness and fastness to perspiration (acidic and alkaline) was studied using standard tests as described in Section 3.3.8. Colour measurements were made before and after reduction clearing to investigate the influence of reduction clearing on the colouristic properties of the fabrics. Specular excluded measurements were carried out initially for the reduction clearing with sodium dithionite only. This was carried out aiming to observe effects on the colouristic properties due to scattering from the dye particles which may adhere to the fabric surface. Measurements were made on the back of the fabric to obviate any variations due to the gloss shown on the face of the fabric. The absorbance of the cold acetone extract of the treated samples was determined for all of the fabric samples in order to quantify the surface dye removal as described in Section 3.3.8. The extinction coefficients of the purified dyes were calculated to determine the concentration of the dye in the acetone extract. This procedure allowed the establishment of the correlation of the surface dye removed with the fastness properties of the dyed samples, provided a measure of the efficiency of reduction clearing and established the validity of the method for the next set of experiments. The assessment of the surface clearing was also made by visualisation of the fabric surface before and after reduction clearing using a scanning electron microscope.

4.4.1 Assessment of Surface Dye Removal

The amount of unfixed superficially attached disperse dye, before and after reduction clearing, was assessed by measuring the absorbance of the cold acetone extract of the treated samples. This method for the removal of surface dye has been described in the literature as an alternative to conventional aqueous reduction clearing [204]. More recently, this method has been used as an alternative to the washfastness tests and to measure the amount of residual unfixed disperse dye on the fabric [196].

Table 4.2 Absorbance values of acetone extracts of all the dyed samples before and after reduction clearing with sodium dithionite

Shade (%)	Dye **1**				Dye **2**				Dye **3**				Dye **4**				Dye **5**			
	Untreated		Reduction cleared		Untreated		Reduction cleared		Untreated		Reduction cleared		Untreated		Reduction cleared		Untreated		Reduction cleared	
	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.
1	439	0.25	433	0.06	511	0.42	510	0.05	512	0.46	511	0.35	631	0.12	628	0.07	666	0.09	666	0.03
2	439	0.55	437	0.08	511	0.86	512	0.12	512	1.17	510	0.73	630	0.26	628	0.15	666	0.22	665	0.04
3	440	1.24	437	0.12	510	1.86	509	0.15	512	1.92	508	0.88	630	0.40	629	0.20	666	0.36	666	0.06
4	440	1.58	438	0.13	511	2.73	507	0.19	511	3.59	509	1.69	630	0.63	630	0.33	665	0.48	665	0.08
5	442	3.00	437	0.12	511	5.49	509	0.28	511	5.43	511	2.36	630	0.86	630	0.75	666	0.88	665	0.10

Table 4.3 Concentration of the dye in the acetone extracts of all the dyed samples before and after reduction clearing with sodium dithionite

Shade (%)	Dye **1**				Dye **2**				Dye **3**				Dye **4**				Dye **5**			
	Untreated		Reduction cleared		Untreated		Reduction cleared		Untreated		Reduction cleared		Untreated		Reduction cleared		Untreated		Reduction cleared	
	λ_{max} (nm)	Conc. (mg l^{-1})	λ_{max} (nm)	Conc. (mg l^{-1})	λ_{max} (nm)	Conc. (mg l^{-1})	λ_{max} (nm)	Conc. (mg l^{-1})	λ_{max} (nm)	Conc. (mg l^{-1})	λ_{max} (nm)	Conc. (mg l^{-1})	λ_{max} (nm)	Conc. (mg l^{-1})	λ_{max} (nm)	Conc. (mg l^{-1})	λ_{max} (nm)	Conc. (mg l^{-1})	λ_{max} (nm)	Conc. (mg l^{-1})
1	439	2.50	433	0.5	511	5.07	510	0.6	512	4.03	511	3.1	631	1.95	628	0.9	666	2.4	666	0.82
2	439	5.52	437	0.8	511	10.4	512	1.4	512	10.2	510	6.4	630	4.2	628	1.95	666	5.4	665	0.91
3	440	12.3	437	1.1	510	22.6	509	1.8	512	16.8	508	7.7	630	7.9	629	2.5	666	8.9	666	1.47
4	440	15.8	438	1.2	511	33.2	507	2.3	511	31.5	509	14.8	630	7.5	630	4.3	665	11.9	665	1.94
5	442	29.9	437	1.1	511	66.9	509	3.4	511	47.6	511	20.7	630	11.4	630	9.6	666	22.0	665	2.48

Since the dyes used were commercial preparations and thus are likely to contain various amounts of auxiliaries such as dispersing agents besides the dye, they were purified for the determination of extinction coefficient. Purification was carried out by extracting with toluene in a Soxhlet apparatus followed by crystallisation. Toluene was selected on the basis of literature precedent and because of its relatively lower toxicity as compared to other potential solvents such as chloroform and benzene.

The absorption maxima in acetone and extinction coefficients of the dyes are given in Table 4.4. It is observed that the ε value for the anthraquinone dyes is significantly less than for the azo dyes.

Table 4.4 Absorption maxima and extinction coefficients of the dyes

Dye	λ_{max} in acetone (nm)	ε x 10^{-4} (g) (l g^{-1} cm^{-1})
1	440	100.2
2	511	82.9
3	512	114.1
4	630	77.9
5	666	40

The acetone extracts were assessed quantitatively by spectrophotometric measurement in the visible region by measuring the absorbance at the absorption maximum for each dye, as given in Table 4.4, with dilution if required. Absorbance values of all the dyed samples before and after reduction clearing with sodium dithionite are given in Table 4.2. A high absorbance value indicates a greater amount of dye present on the surface of the sample. Samples with absorbance values greater than 2 were diluted appropriately and the absorbance value adjusted accordingly. The absorbance values were used to calculate the concentration of dye in the acetone extract using the Beer Lambert law, written as Equation 4.1.

$$A = \varepsilon . l . c \qquad (4.1)$$

Where, A = absorbance

ε = absorptivity or absorption coefficient, l g^{-1} cm^{-1}

l = length of the light path, cm

c = concentration of the dye, g l^{-1}

The amount of extracted dye is expressed as the concentration of dye in the acetone extracts, calculated on the basis of extinction coefficients measured for purified samples of the dyes, for each dyed fabric before and after reduction clearing, as illustrated in Figures 4.2 - 4.6 and tabulated in Table 4.3. In each case, the figures illustrate the expected progressive increase in the level of surface dye with increasing depth of shade, and also that reduction clearing results in significant removal of surface dye. There is a higher level of surface dye before clearing in the case of azo dyes **1**-**3**, compared with anthraquinones **4** and **5**, with dye **2** giving the highest value. It is clear that reduction clearing is relatively efficient in the case of dyes **1**, **2** and **5** (Figures 4.2, 4.3 and 4.6 respectively).

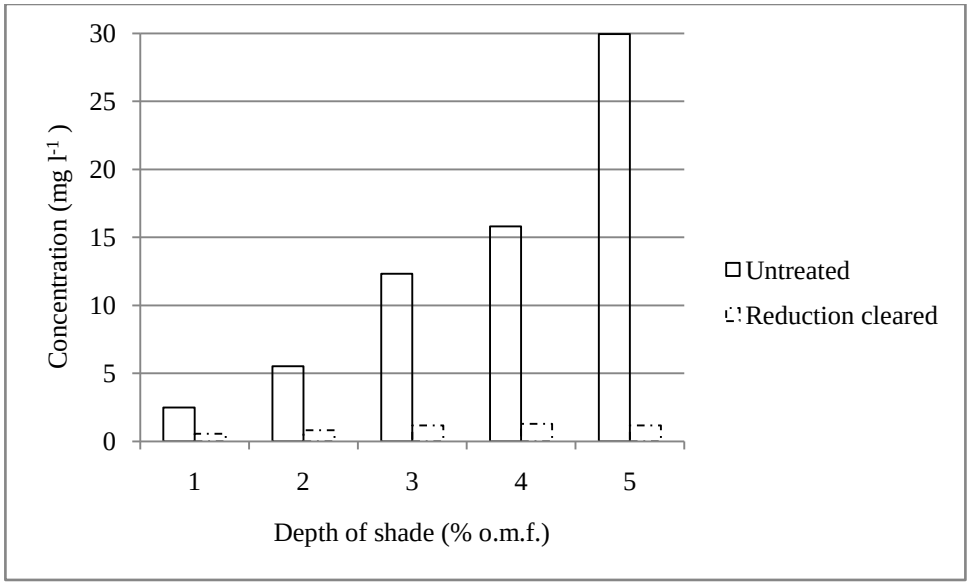


Figure 4.2 Concentration of dye **1** in the acetone extract before and after reduction clearing with sodium dithionite

As illustrated in Figure 4.4, conventional reduction clearing is much less efficient in the case of dye **3**, which is structurally similar to dye **2** but with no ester groups**.** Thus, the presence of the ester groups in dye **2**, offering the additional possibility of hydrolysis under alkaline conditions which would lead to a much more hydrophilic dye structure in which the ester group is replaced by a hydroxyl group, appears to facilitate the clearing process.

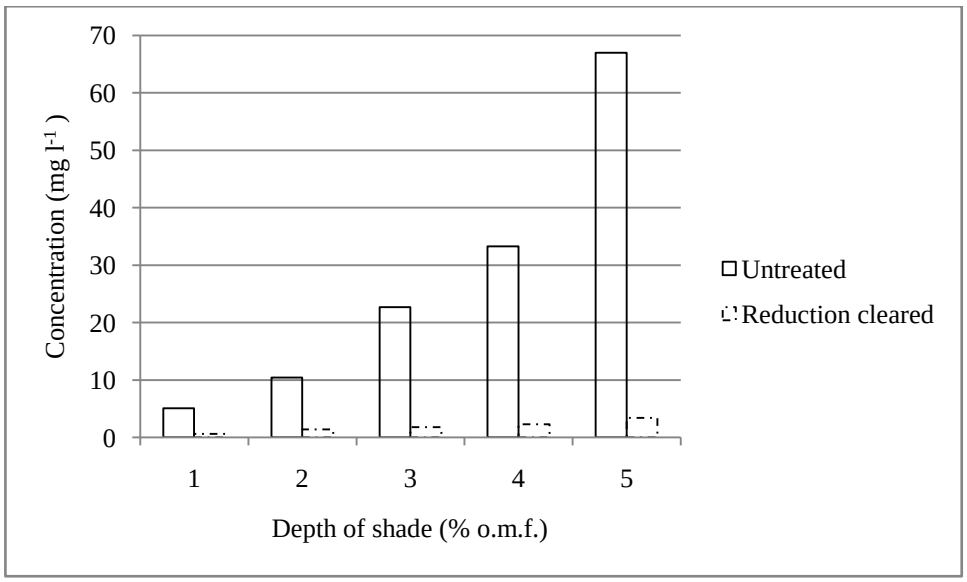


Figure 4.3 Concentration of dye **2** in the acetone extract before and after reduction clearing with sodium dithionite

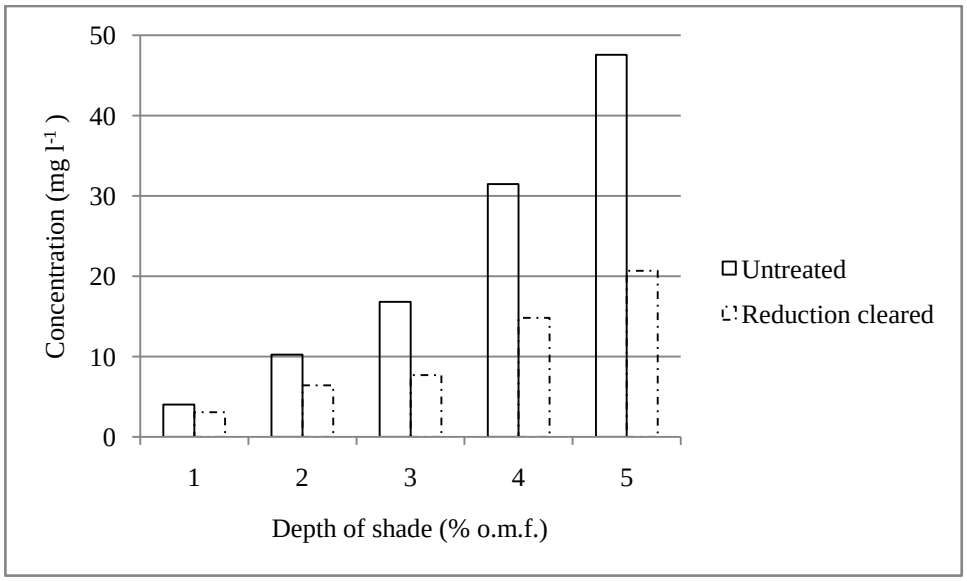


Figure 4.4 Concentration of dye **3** in the acetone extract before and after reduction clearing with sodium dithionite

Reduction clearing is also inefficient in the case of dye **4** as indicated by a higher concentration of dye in the acetone extract after reduction clearing (Figure 4.5).

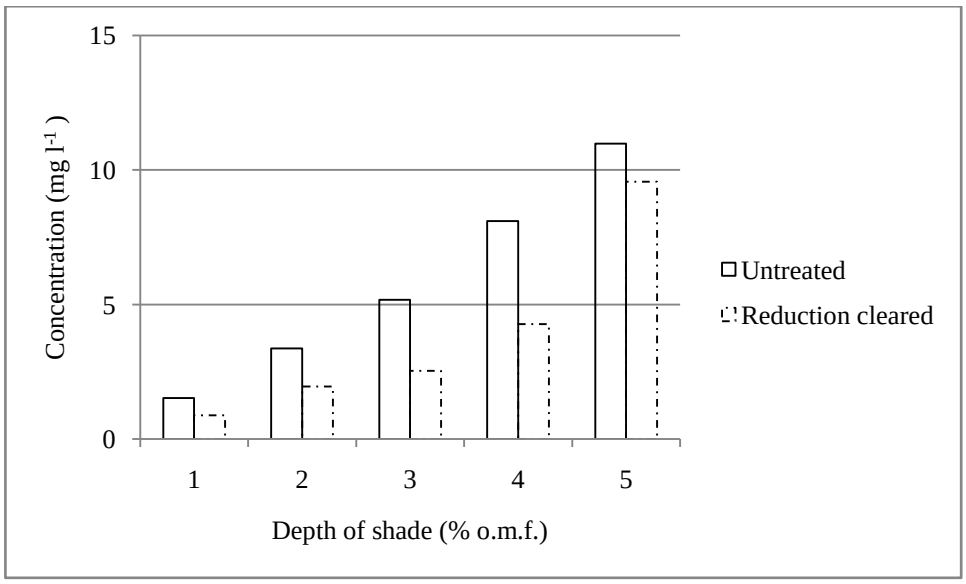


Figure 4.5 Concentration of dye **4** in the acetone extract before and after reduction clearing with sodium dithionite

The absorbance values given by dyes **1** and **2** before reduction clearing increase to values higher than 1 at depths of 3, 4 and 5% that is, at medium to high depths of shade. The absorbance value given by dye **3** is higher than 1 even at 2% depth while the blues, dye **4** and dye **5** give absorbance values less than 1 even at 5% depth. The lower absorbance values of anthraquinone dyes may be attributed in part to their lower extinction coefficients. However, the concentration of anthraquinone based dyes is also comparatively lower than those of the azo dyes as shown in Table 4.3.

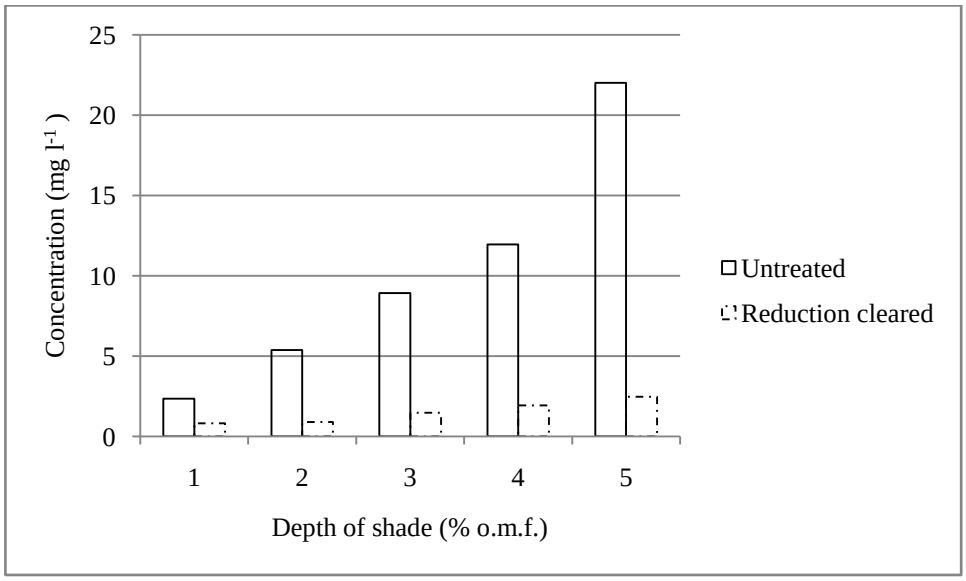


Figure 4.6 Concentration of dye **5** in the acetone extract before and after reduction clearing

The absorbance values before reduction clearing given by dyes **4** and **5** are comparable to each other while their concentrations differ significantly as the depth of shade increases. Dye **4** gives the lowest concentration among the selected dyes in acetone extract before reduction clearing. It is also noted that dye **4** is a mixture of two structures. It also behaved differently during Soxhlet extraction in that it took a longer time period for extraction than the other dyes (Section 3.3.8).

The observed general trend is that the concentration of extracted dye increases as the depth of shade increases. This indicates the deposition of a higher amount of unfixed dye on the surface of the sample as the depth of dyeing is increased. In the case of dye **1** and dye **2**, sodium dithionite removes quite significant amounts of surface dye, as can be seen in Figures 4.2 and 4.3. In contrast, in the case of dye **3**, sodium dithionite is able to remove only a small amount of unfixed surface dye and much of the dye remains on the surface (Figure 4.4). However, at higher depths of shade of fabrics dyed with dye **3**, the amount of surface dye removed increases and about 50% of the unfixed surface dye is removed at 5% depth of shade. Dye **2** and dye **3** have similar structures and the absorbance value given by the acetone extract of the untreated samples is also similar, but after reduction clearing the absorbance values given by the acetone extract of the fabrics dyed with the two dyes are quite different (Table 4.3). This difference appears to be associated with the different pendant groups on the two dyes; dye **2** has two potentially hydrolysable ester groups, which appear to cause it to be more susceptible to alkaline reduction clearing, possible because it enhances water-solubility thus becoming more accessible to the reducing agent and thus give lower absorbance values indicating enhanced removal of surface dye.

The amount of surface dye as assessed by the concentration of the dye in the cold acetone extract of the fabrics dyed with dyes **4** and **5** before reduction clearing is similar at lower depths of shade only and the difference increases at higher depths of shade, i.e., at 4 and 5% o.m.f. (Table 4.3). However after reduction clearing with sodium dithionite, the difference between the amount of residual surface dye on the sampled dyed with the two blue dyes (**4** and **5**) increases. In the case of dye **5**, reduction clearing removes a greater amount of superficial dye while in the case of dye **4** only a small amount of surface dye is removed. Both the blue dyes contain an anthraquinone chromophore; however, dye **4** is a mixture of two anthraquinone structures. The lower response of dye **4** to reduction may be due to the presence of four strongly electron-releasing groups (OH, NH_2) in the anthraquinone nucleus in contrast to dye **5** which has only two electron-releasing substituent groups (Figure 4.1).

The increase in electron density in the chromophoric system of dye **4** may contribute to its resistance to reduction.

The data for the concentration of dyes in acetone extract (Table 4.4) shows that after reduction clearing the concentration of most of the dyes, dye **1**, **2** and **3** is below 4 mg l^{-1} even at the highest depth of shade studied. Whereas the dyes for which the degree of surface dye removal is relatively less, which are dyes **3** and **4**, the concentration of dye in the acetone extract after reduction clearing is greater than 4 mg l^{-1} even more than 10 mg l^{-1} in the case of dye **3**. In the case of dye **2**, the effect of reduction clearing is quite remarkable, for example, at 5% depth of shade, the concentration of dye in the acetone extract decreases from 67 mg l^{-1} to 3.4 mg l^{-1}. This can be attributed to the presence of the ester groups in dye **2** (Figure 4.1) which is hydrolyzed by alkali, thus making the dye removal easier.

Anthraquinone dyes are generally said to be resistant to reduction/degradation and they remain colored for longer periods than other dye classes [205]. However, only one of the two anthraquinone dyes used in this study follows this generality. Dye **5** is efficiently removed whereas dye **4** does not respond well to reduction clearing.

Figures 4.2 – 4.6 clearly show the correlation between the concentrations in the acetone extract with the depth of shade. It is observed that there is an almost linear relationship between the absorbance value and the depth of shade of a dye before reduction clearing. It also leads to the conclusion that acetone extract of the treated samples is a valid test for the assessment of unfixed dye present on the surface of the samples.

4.4.2 Washfastness Properties after Reduction Clearing with Sodium Dithionite

The results of washfastness tests for all the samples dyed with all of the dyes at all five depths of shade before and after reduction clearing with sodium dithionite are shown in Table 4.5.

Table 4.5 Washfastness properties of the dyed samples before and after reduction clearing with sodium dithionite

		Shade (%)	Change in colour	Staining					
				Wool	Acrylic	PET	Nylon	Cotton	Acetate
Dye **1**	Untreated	1	5	5	5	5	4-5	5	5
		2	5	5	5	5	4-5	5	4-5
		3	5	5	5	5	4	5	4
		4	5	5	5	5	3-4	5	3-4
		5	5	4-5	5	4-5	3	5	3
	Reduction cleared	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5
Dye **2**	Untreated	1	5	4-5	5	4-5	3-4	4-5	2-3
		2	5	4	4-5	3-4	3	4-5	2
		3	5	4	4-5	3	2-3	4-5	1-2
		4	4-5	3	4-5	2-3	2	4-5	1-2
		5	4-5	3	4-5	2-3	2	4	1-2
	Reduction cleared	1	4-5	5	5	5	5	5	5
		2	4-5	5	5	5	5	5	5
		3	4-5	5	5	5	5	5	4-5
		4	4-5	5	5	5	4-5	5	4-5
		5	4-5	5	5	5	4-5	5	4-5
Dye **3**	Untreated	1	5	4-5	5	4-5	4	5	3-4
		2	5	4-5	5	4	2-3	5	2-3
		3	4-5	4	5	3-4	2-3	5	2-3
		4	4-5	3-4	4-5	3	2	4-5	2
		5	4-5	3	4-5	3	1-2	4-5	1-2
	Reduction cleared	1	5	5	5	4-5	4-5	5	4-5
		2	4-5	5	5	4-5	3-4	5	3-4
		3	4-5	4-5	5	4	3-4	5	3-4
		4	4-5	4	4-5	4	3	4-5	3
		5	4-5	4	4-5	3-4	3	4-5	3

		Shade (%)	Change in colour	Staining					
				Wool	Acrylic	PET	Nylon	Cotton	Acetate
Dye **4**	Untreated	1	4-5	4-5	5	4-5	3-4	4-5	4-5
		2	4-5	4-5	5	4-5	3	4-5	4
		3	4-5	4	5	4	2-3	4-5	3-4
		4	4-5	4	4-5	4	2	4-5	3-4
		5	4-5	3-4	4-5	3-4	1-2	4-5	3
	Reduction cleared	1	4-5	5	5	5	4-5	5	5
		2	4-5	5	5	4-5	4	5	4-5
		3	4-5	4-5	5	4-5	3-4	5	4-5
		4	4-5	4-5	5	4-5	3	5	4-5
		5	4-5	4-5	5	4	2-3	5	4
Dye **5**	Untreated	1	4	4-5	5	5	5	5	5
		2	4-5	4-5	5	5	5	5	5
		3	4-5	4-5	5	5	5	5	5
		4	4-5	4-5	5	5	5	5	5
		5	4-5	4-5	5	5	5	5	5
	Reduction cleared	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5

Washfastness properties are described by two parameters, one is the change in the colour of the dyed sample and the other is the staining of the adjacent fabric. The change in shade of the sample is assessed by comparison with a grey scale for change in colour and the degree of staining is assessed by the grey scale for staining. The ratings for change in colour range from 1 to 5. Rating 1 indicates the greatest loss of colour and this loss decreases as the rating value increases, with 5 representing no change in colour. Similarly the scales for staining start from 1 for deep staining (poor washfastness) to 5 for no staining (excellent washfastness) [2].

It is clear from Table 4.5 that the dyed samples have very good washfastness properties, if judged solely on the basis of the change in colour. However, the staining on the adjacent multifibre fabric gives different results. In this research, the adjacent fabric for used in

washfastness tests was a multifibre fabric (SDC). Multifibre fabric is composed of six different fibre types which are wool, acrylic, polyester, nylon, cotton and acetate in that order.

The results in Table 4.5 show that acrylic and cotton are not stained by any of the dyed samples whereas acetate and nylon are the most highly stained among the six fibre types followed by polyester and wool. This can be explained on the basis that the disperse dyes have higher affinity for acetate and nylon. Thus any superficial dye removed which has not undergone reduction has more tendency to stain these fibres. In fact, at lower temperatures, disperse dyes have higher affinity for nylon than polyester and this is a major reason for the pronounced staining of nylon during the washfastness test.

Consequently, it is evident that washfastness properties are influenced by the efficiency of the clearing process as well as the inherent affinity of the dye for the test fibre as well as for the adjacent fibre. Accordingly, staining on nylon and acetate can be considered as the most useful parameter among the six fibre types for assessing the efficiency of reduction clearing by providing clear discrimination. It is observed that the staining of the multifibre fabric becomes deeper as the depth of shade is increased, that is the washfastness properties deteriorate at higher depths of shade. Dye **1** only gives slight staining at low depths of shade, that is a rating of 4-5 at 1% and 2% depths of shade. At higher depths of shade the staining deepens to give a rating of 3. However reduction clearing with sodium dithionite improves the stain rating to 5 even at 5% depth of shade. Dye **2** gives poor washfastness properties before clearing if judged from the staining of multifibre fabric. It produces deep stains, rating 1-2 on acetate at medium to high depths of shade. However, in this case too, reduction clearing with sodium dithionite improves the stain rating to 4-5, that is, the washfastness is improved to very good from poor. Similar to dye **2**, dye **3** also gives poor washfastness properties with staining of rating 1-2 at 5% depth of shade. However, in the case of dye **3**, reduction clearing with sodium dithionite only improves the stain rating to 3, that is, the washfastness is improved to only medium from poor. Dyes **2** and **3** both have very similar structures with the difference being the presence of the acetyl groups as side-chain substituents on dye **2**, compared with ethyl and cyano groups on dye **3**. However, this seemingly small structural difference means that the response of the two dyes to clearing is very different and thus also the washfastness properties. The presence of acetyl groups

renders dye **2** susceptible to hydrolysis. Although its reduction is not facilitated in comparison with dye **3**, the new dye structure which is formed from hydrolysis contains hydroxyl groups in place of the ester group and this is comparatively easier to remove because of its potential hydrophilicity, easier to be rinsed off and hence removed under reduction clearing conditions.

Dye **4** gives poor staining on nylon, that is, a rating 1-2 at 5% depth of shade. Reduction clearing only improves the stain rating to 2-3, indicating medium washfastness properties. This result is in agreement with the percentage of surface dye removed as discussed in Section 4.4.1. Dye **4** was the only dye among the five selected dyes which gave progressively lower efficiency of dye removal as the depth of shade increased. As shown in Table 4.5, dye **5** has excellent washfastness properties, that is there is no staining at all of any component fibre of the multifibre fabric and only a slight change in colour, as indicated by a rating of 4-5. The absence of staining of the adjacent multifibre fabric points to two possibilities. Firstly, there is no or very little surface dye present on the fabrics dyed with dye **5**. Secondly, there is some superficial dye that has come off during washfastness test but it has not been taken up by any component of the multifibre fabric. The data in Table 4.3 shows that there is certain amount of surface dye on samples dyed with dye **5** which is extracted by acetone. For example, 22 mg l^{-1} of dye **5** is present in the acetone extract of the samples dyed at 5% depth of shade. Although the amount of extracted dye is comparatively less than the azo dyes (for example, 67 mg l^{-1} of dye **2** at 5% depth of shade), it is higher than the amount of extracted dye from samples dyed with dye **4** (which was only 11.4 mg l^{-1} at 5% depth of shade). Dye **5** has been described by the suppliers as a high energy dye, that is, it requires higher temperatures for application. Thus, it appears more a plausible proposal that any dye that has been removed during washfastness test is not taken up by the adjacent fibres under the conditions of washfastness test.

Reduction clearing with sodium dithionite improves the washfastness properties of the dyed fabrics significantly, except for dyes **3** and **4**. These are also the two dyes that responded poorly to surface dye removal by reduction clearing as discussed in Section 4.4.1. These results lead to the conclusion that the clearing efficiency varies with the particular dye. The type of the chromophore may be one of the factors which influence the clearing efficiency but a generalization on the basis of chromophore cannot be made. However, generally, reduction clearing has positive influence on the washfastness properties of the dyed fabrics.

4.4.3 Rubfastness Properties after Reduction Clearing with Sodium Dithionite

Rubfastness was assessed by staining on white cotton when rubbed under test conditions against the dyed fabric. Dry and wet fastness to rubbing of all the dyed samples before and after reduction clearing with sodium dithionite is given is Table 4.6.

Rubfastness of fabrics dyed with dyes **1** – **4** before reduction clearing is unsatisfactory especially at high depths of shade and the ratings decrease with an increase in depth of shade. Wet rubfastness of fabrics dyed with dyes **2** and **4** is slightly inferior to the dry rubfastness and the reverse is the case for the samples dyed with dyes **1** and **3**. However reduction clearing with sodium dithionite improves the rubfastness of all the dyed samples to very good – excellent (stain rating of 4-5 to 5). Rubfastness of fabrics dyed with dye **5** is excellent, as indicated by a stain rating of 5, even before reduction clearing and thus it cannot be improved further.

Table 4.6 Rubfastness of the dyed samples before and after reduction clearing with sodium dithionite

	Shade (%)	Dye **1**		Dye **2**		Dye **3**		Dye **4**		Dye **5**	
		Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Untreated	1	5	5	4-5	4-5	4-5	5	4-5	4-5	5	5
	2	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5	5
	3	4-5	4-5	4	4	4	4-5	4-5	4	5	5
	4	4	4-5	4	3-4	3-4	4	4-5	4	5	5
	5	3-4	4	3-4	3	3-4	4	3-4	3-4	5	5
Reduction cleared	1	5	5	5	5	5	5	5	5	5	5
	2	5	5	5	5	4-5	5	5	5	5	5
	3	5	5	5	5	4-5	5	5	5	5	5
	4	5	5	5	5	4-5	5	5	5	5	5
	5	5	5	5	5	5	5	5	4-5	5	5

4.4.4 Perspiration Fastness after Reduction Clearing with Sodium Dithionite

Fastness to acidic and alkaline perspiration of all the dyed samples before and after reduction clearing is shown in Table 4.7 and Table 4.8.

Table 4.7 Fastness of the dyed samples to acidic perspiration before and after reduction clearing with sodium dithionite

		Shade (%)	Change in colour	Staining					
				Wool	Acrylic	PET	Nylon	Cotton	Acetate
Dye **1**	Untreated	1	5	5	5	5	5	5	5
		2	5	5	5	5	4-5	5	5
		3	5	4-5	4-5	4-5	4-5	5	4-5
		4	5	4-5	4-5	4-5	4-5	5	4-5
		5	5	4-5	4-5	4-5	4-5	5	4-5
	Reduction cleared	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5
Dye **2**	Untreated	1	5	4-5	4-5	4-5	4	4-5	4
		2	5	4-5	4-5	4	4	4-5	4
		3	5	4-5	4-5	4	3-4	4-5	3-4
		4	5	4-5	4-5	4	3-4	4-5	3-4
		5	5	4-5	4-5	4	3-4	4-5	3-4
	Reduction cleared	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5
Dye **3**	Untreated	1	5	5	5	4-5	4-5	5	5
		2	5	5	5	4-5	4	5	5
		3	5	4-5	4-5	4	3-4	4-5	4-5
		4	5	4-5	4-5	4	3-4	4-5	4-5
		5	5	4-5	4-5	4	3	4-5	4
	Reduction cleared	1	5	5	5	5	5	5	5
		2	5	5	5	5	4-5	5	5
		3	5	5	5	4-5	4-5	5	4-5
		4	5	4-5	4-5	4-5	4	5	4-5
		5	5	4-5	4-5	4-5	4	5	4-5

		Shade (%)	Change in colour	Staining					
				Wool	Acrylic	PET	Nylon	Cotton	Acetate
Dye **4**	Untreated	1	5	4-5	5	4-5	5	5	5
		2	5	4-5	4-5	4-5	5	5	5
		3	4-5	4-5	4-5	4-5	5	5	5
		4	4-5	4-5	4-5	4-5	5	5	5
		5	4-5	4-5	4-5	4-5	4-5	5	5
	Reduction cleared	1	5	5	5	5	5	5	5
		2	4-5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	4-5	5	5	5	5	5	5
		5	5	4-5	5	4-5	4-5	5	5
Dye **5**	Untreated	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5
	Reduction cleared	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5

Fastness to perspiration is also assessed by two parameters, change in colour of the dyed sample and staining of the adjacent fabric. In this case, the adjacent fabric is multifibre fabric. Similar to the washfastness test, the staining in the perspiration fastness test is more important than the change in the colour of the fabric. Nylon and acetate are the most deeply stained fibres of the multifibre fabric.

Table 4.8 Fastness of the dyed samples to alkaline perspiration before and after reduction clearing with sodium dithionite

		Shade (%)	Change in colour	Staining					
				Wool	Acrylic	PET	Nylon	Cotton	Acetate
Dye **1**	Untreated	1	5	5	5	4-5	4-5	5	4-5
		2	5	5	4-5	4	4	5	4
		3	5	4-5	4-5	4	4	5	4
		4	5	4-5	4-5	4	4	5	4
		5	5	4-5	4-5	4	4	5	4
	Reduction cleared	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5
Dye **2**	Untreated	1	5	4-5	4-5	4-5	4-5	4-5	4-5
		2	5	4-5	4-5	4-5	4	4-5	4-5
		3	5	4-5	4-5	4	4	4-5	4
		4	5	4-5	4	4	3-4	4-5	4
		5	5	4-5	4	3-4	3	4-5	3-4
	Reduction cleared	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5
Dye **3**	Untreated	1	5	5	5	4-5	4-5	5	5
		2	5	4-5	4-5	4	4	5	4-5
		3	4-5	4-5	4-5	4	3-4	4-5	4-5
		4	4-5	4-5	4-5	4	3-4	4-5	4
		5	4-5	4	4	3-4	3	4	3-4
	Reduction cleared	1	5	5	5	5	5	5	5
		2	5	5	5	4-5	4-5	5	5
		3	5	5	5	4-5	4-5	5	5
		4	5	5	5	4-5	4	5	4-5
		5	5	4-5	4-5	4	4	4-5	4-5

		Shade (%)	Change in colour	Staining					
				Wool	Acrylic	PET	Nylon	Cotton	Acetate
Dye **4**	Untreated	1	5	4-5	4-5	4-5	4	4-5	4-5
		2	5	4-5	4-5	4-5	4	4-5	4-5
		3	4-5	4-5	4-5	4-5	4	4-5	4-5
		4	5	4-5	4-5	4-5	4	4-5	4-5
		5	5	4-5	4-5	4-5	3-4	4	4-5
	Reduction cleared	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	4-5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5
Dye **5**	Untreated	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5
	Reduction cleared	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5

The perspiration fastness properties of the dyed fabrics show similar trends to the washfastness properties. Thus, samples dyed with dye **3** respond relatively poorly than the rest of the dyed samples and the fastness to perspiration of the fabric dyed with dye **3** is improved to a stain rating of 4 only. However, the fastness to perspiration of all the dyed fabrics is improved to very good after reduction clearing with sodium dithionite. It is observed from Tables 4.7 and 4.8 that the fastness to acidic and alkaline perspiration is similar to each other. Fastness of the fabrics dyed with dye **4** to alkaline perspiration is slightly lower than fastness to acidic perspiration. However, reduction clearing with sodium dithionite improves the fastness to alkaline perspiration from a stain rating of 3-4 to 5. Overall, fastness to perspiration of all the dyed samples is in agreement with the washfastness properties.

4.4.5 Colour Properties after Reduction Clearing with Sodium Dithionite

The colour of an object can be described by three attributes which are hue, saturation and lightness. The description of the colour properties has been standardized by using various colour models which define a colour numerically. The colour model and tolerance system used in this study are CIELAB and CMC respectively. CIELAB is based on the values L*, a* and b* while CMC is a colour difference system based on L*, C* and h°. In these models, L* represents lightness, a* red/green, b* yellow/blue, C* chroma and h° symbolizes hue angle. Hue angle is measured in degrees around a circle, where 0° is red, 90° is yellow, 180° is green and blue is 270°. Chroma defines the saturation level of a particular hue. It is a measure of the distance of a particular hue from a neutral in the colour space which has same lightness. Lightness measures the closeness of a colour to white. It is a perception of the reflectance or the amount of light reflected from a surface by which white objects are distinguished from grey and light coloured objects from dark. A higher value of L* indicates a light colour and a low value of lightness indicates a dark colour. Rather than using K/S (Kubelka Munk function) values, integ values are used in this research as a measure of colour strength. The integ value is the colour yield of the dye and represents the apparent colour strength. It is a more accurate parameter to relate the colour intensity of an opaque object to the applied concentration of the dye. Integ values are obtained by the integration of the Kubelka-Munk constant where K/S at each wavelength is scaled / weighted by the standard observer and light source at that wavelength. This is more helpful than K/S as the maximum absorption tends to shift at higher depths of shade [206-208].

The colour properties of the dyed samples before and after reduction clearing with specular reflection included are given in Tables 4.9 – 4.13. The colour differences between the untreated and the reduction cleared samples are shown in Table 4.14.

The lightness of the fabrics dyed with dye **1** increases after reduction clearing at all depths of shade as indicated by the L* values given in Table 4.9. This increase becomes significant at higher depths of shade ($\Delta L^* > 1$, Table 4.14).

Table 4.9 Colour measurements of the samples dyed with dye **1** before and after reduction clearing with sodium dithionite

Shade		L*	a*	b*	C*	h°	Integ value
1 %	Untreated	83.32	9.0	104.69	105.08	85.09	22.39
	Reduction cleared	84.14	8.9	105.95	106.32	85.20	22.29
2 %	Untreated	80.76	14.36	104.64	105.62	82.19	26.82
	Reduction cleared	81.79	14.68	106.41	107.41	82.15	26.93
3 %	Untreated	78.62	17.67	102.31	103.83	80.2	27.83
	Reduction cleared	79.78	18.08	104.66	106.21	80.2	28.59
4 %	Untreated	77.14	19.37	100.36	102.21	79.07	28.22
	Reduction cleared	78.39	19.77	102.79	104.67	79.11	28.86
5 %	Untreated	77.05	20.02	100.44	102.41	78.73	28.48
	Reduction cleared	78.17	20.62	102.62	104.67	78.64	29.04

For samples dyed with dye **1**, the *a** value shows a slight increase while the increase in *b** value is quite high and regular (Table 4.9). The *h*° values of samples dyed with dye **1** do not show a regular trend after reduction clearing and the only significant change is observed at 3% depth of shade (Table 4.14).

Table 4.10 Colour measurements of the samples dyed with dye **2** before and after reduction clearing with sodium dithionite

Shade		L*	a*	b*	C*	h°	Integ value
1 %	Untreated	31.81	43.59	3.67	43.75	4.82	27.99
	Reduction cleared	32.17	45.13	3.74	45.28	4.73	28.02
2 %	Untreated	26.95	38.61	6.36	39.13	9.35	41.02
	Reduction cleared	27.06	39.79	6.15	40.26	8.79	41.38
3 %	Untreated	24.59	34.05	7.14	34.79	11.84	47.58
	Reduction cleared	24.4	34.94	6.76	35.59	10.95	48.9
4 %	Untreated	23.32	30.71	7.33	31.57	13.42	51.07
	Reduction cleared	23.18	31.92	6.87	32.65	12.15	52.19
5 %	Untreated	22.46	27.45	7.11	28.35	14.52	54.02
	Reduction cleared	22.09	29.02	6.43	29.73	12.5	54.93

The lightness of samples dyed with dyes **2** and **3** show some irregular behaviour according to Table 4.10 and Table 4.11. In the case of samples dyed with dye **2**, *L** value increases slightly for 1% and 2% depth of shade and then decreases for higher depths of shade. Sampled dyed with dye **3** show a similar trend with *L** value increasing slightly for shades of 1% and then decreases at higher depths of shade, that is at, 2, 3,4, and 5%. However, the change is quite insignificant at lower depths of shade.

The *a** value of samples dyed with dye **2** increases after reduction clearing (Table 4.10). At the same time the *b** value shows a decrease except at 1% depth of shade, where the change is negligible ($\Delta b^* = 0.06$). The decrease in *h*° value and b* value after reduction clearing indicates a shift of colour towards blue. The presence of potentially hydrolysable ester groups in the side chain of dye **2** may result in a slight bathochromic shift in the colour of the dye. However, it is highly improbable that sodium dithionite or alkali would hydrolyse the dye during reduction clearing that has penetrated inside the fibre.

However, in a similar manner, the *h*° value and b* value of the samples dyed with dye **3** decreases after reduction clearing (Table 4.11) indicating a slight shift towards blue. Thus, even without the presence of any hydrolysable group, dye **3** undergoes a shift in the maximum absorption which appears as a shift towards blue.

Table 4.11 Colour measurements of the samples dyed with dye **3** before and after reduction clearing with sodium dithionite

Shade		L*	a*	b*	C*	h°	Integ value
1 %	Untreated	30.21	44.48	7.26	45.07	9.27	35.02
	Reduction cleared	30.31	45.02	7.11	45.58	8.97	35.07
2 %	Untreated	25.34	36.92	8.68	37.93	13.23	48.19
	Reduction cleared	25.25	37.62	8.42	38.55	12.62	48.99
3 %	Untreated	23.27	32.12	8.5	33.23	14.82	53.79
	Reduction cleared	23.13	32.91	8.29	33.93	14.14	54.98
4 %	Untreated	21.99	28.3	7.9	29.38	15.59	56.79
	Reduction cleared	21.52	28.59	7.62	29.59	14.93	59.35
5 %	Untreated	21.14	24.44	7.28	25.51	16.58	57.93
	Reduction cleared	20.79	26.01	7.09	26.96	15.25	60.8

Table 4.12 Colour measurements of the samples dyed with dye **4** before and after reduction clearing with sodium dithionite

Shade		L*	a*	b*	C*	h°	Integ value
1%	Untreated	33.68	-0.37	-36.72	36.72	269.43	19.69
	Reduction cleared	32.61	0.52	-36.75	36.75	270.81	21.12
2%	Untreated	25.01	4.93	-33.05	33.42	278.49	33.33
	Reduction cleared	26.6	4.04	-34.51	34.75	276.68	30.81
3%	Untreated	21.48	6.73	-29.26	30.02	282.96	40.17
	Reduction cleared	23.99	5.52	-32.58	33.04	279.62	35.67
4%	Untreated	20.21	7.02	-26.98	27.87	284.58	42.88
	Reduction cleared	20.88	6.81	-28.56	29.36	283.41	41.82
5%	Untreated	19.29	7.06	-25.28	26.25	285.61	45.33
	Reduction cleared	19.84	6.91	-26.49	27.37	284.62	44.12

There is no particular trend observable in the change in the lightness of samples dyed with dye **4** after reduction clearing except that the change decreases in magnitude at higher depths of shade which is quite different to the trends seen with the other dyes. However, the change in chroma is greater at higher depths of shade (Table 4.12). Chroma increases after reduction clearing indicating that reduction clearing increases the saturation of samples dyed with dye **4** thus making them more vivid. The change in hue again decreases with increase in depth of shade, as does the change in integ value and the colour difference. This may be expected from the percentage of surface dye removal as measured from the concentration of dye in cold acetone extract (Table 4.3) which shows a decrease as the depth of shade increases. It is to be noted that among the five selected dyes, only dye **4** behaves in this manner.

The colour measurements for samples dyed with dye **5** as shown in Table 4.13 indicate that there is only a slight change in lightness as was observed for samples dyed with dyes **2** and **3**. The change in lightness of the samples dyed with dye **5** remains more or less constant at all depth of shade whereas the change in lightness of samples dyed with dye **4** is quite significant at lower depths of shade and becomes comparable to that of dye **5** at higher depths of shade.

Table 4.13 Colour measurements of the samples dyed with dye **5** before and after reduction clearing with sodium dithionite

Shade		L*	a*	b*	C*	h°	Integ value
1 %	Untreated	54.25	-19.44	-30.52	36.19	237.5	6.01
	Reduction cleared	54.52	-18.41	-33.77	38.47	241.4	6.13
2 %	Untreated	45.37	-16.1	-33.06	36.77	244.04	11.6
	Reduction cleared	45.98	-15.57	-35.09	38.39	246.07	11.49
3 %	Untreated	40.82	-13.57	-33.99	36.6	248.24	15.8
	Reduction cleared	40.88	-12.56	-35.18	37.35	250.35	15.78
4 %	Untreated	37.2	-10.72	-34.05	35.69	252.52	19.3
	Reduction cleared	37.3	-9.86	-35.45	36.8	254.45	19.47
5 %	Untreated	34.16	-7.89	-34.12	35.02	256.98	22.65
	Reduction cleared	34.32	-7.28	-35.11	35.85	258.28	22.66

The chroma of all the dyed samples shows a marked increase after reduction clearing as indicated by ΔC* values given in Table 4.14. Samples dyed with dye **1** show the highest and most regular change in saturation, with higher values for higher depths of shade. Samples dyed with dye **5** behave in a directly opposite manner, showing a lower increase in saturation at higher depths of shade, while dye **3** does not show a noticeable change in saturation as indicated by the change in chroma (Table 4.14).

A general intuitive expectation might be an increase in colour differences before and after reduction clearing with an increase in depth of shade as the amount of surface dye removed is increased. However, in the case of samples dyed with dye **5**, colour differences behave in an opposite manner with differences becoming smaller at higher depths of shade when the percentage of surface dye removed is increasing. This implies that in practice, it appears that the colour properties cannot be judged or estimated on the basis of surface dye removed as the colour properties depend on the dye remaining on the fabric.

Table 4.14 Colour differences of all the dyed samples after reduction clearing with sodium dithionite

	Shade (%)	ΔL*	Δa*	Δb*	ΔC*	ΔH*	ΔE (CMC)	Change in integ value
Dye **1**	1	0.81	-0.1	1.26	1.25	0.21	0.48	-0.1
	2	1.03	0.32	1.77	1.79	-0.08	0.64	0.11
	3	0.15	1.65	1.16	1.43	-1.43	0.89	1.47
	4	1.25	0.39	2.43	2.46	0.07	0.86	0.64
	5	1.12	0.6	2.19	2.26	-0.16	2.53	0.56
Dye **2**	1	0.37	1.53	0.06	1.53	-0.07	0.67	0.03
	2	0.11	1.18	-0.21	1.13	-0.39	0.56	0.36
	3	-0.14	1.68	-0.17	1.61	-0.51	0.84	2.02
	4	-0.14	1.21	-0.46	1.08	-0.71	0.77	1.12
	5	-0.37	1.57	-0.68	1.37	-1.02	1.13	2.27
Dye **3**	1	0.1	0.54	-0.15	0.51	-0.24	0.26	0.05
	2	-0.08	0.7	-0.26	0.62	-0.41	0.4	0.8
	3	-0.12	0.9	-0.05	0.86	-0.27	0.46	1.32
	4	-0.47	0.3	-0.27	0.22	-0.34	0.47	2.56
	5	-0.35	1.57	-0.19	1.45	-0.61	0.99	2.87
Dye **4**	1	-1.07	0.89	-0.03	0.03	0.89	0.91	1.43
	2	1.59	-0.89	-1.45	1.32	-1.07	1.55	-2.52
	3	0.26	0.15	-0.48	0.5	0.05	0.32	-0.65
	4	0.67	-0.21	-1.58	1.48	-0.58	1.08	-1.06
	5	0.55	-0.16	-1.21	1.12	-0.47	0.87	-1.21
Dye **5**	1	0.3	1.03	-3.25	2.3	2.5	2.0	0.1
	2	0.6	0.53	-2.03	1.6	1.3	1.2	-0.1
	3	0.56	1	-0.96	0.56	1.27	0.94	-0.68
	4	0.1	0.86	-1.41	1.1	1.2	1.0	0.2
	5	0.2	0.61	-0.99	0.8	0.8	0.7	0.01

The integ value, which indicates the visual colour strength of the dyed sample as it appears to the eye, does not show much change in the case of dye **5**. For samples dyed with dye **2**, it shows a slight increase for 1% and 2% depths of shade but increases markedly for depths of shade 3, 4 and 5%. The integ value of samples dyed with dyes **1** and **3** also increases after reduction clearing. In the case of dye **3**, the change is small for pale depths but a uniform and regular increasing change is observed at higher depths of shade. Samples dyed with dye **1** behave in a similar manner but to a lesser degree. The integ value of dye **3** and dye **4** is affected the most by reduction clearing while that of dye **5** experiences the lowest influence. It is quite interesting in that dyes **3** and **4** are the two dyes for which reduction clearing is unable to remove much of the surface dye as shown by the percentage of dye removed by cold acetone extract.

Light reflected from an opaque material such as a textile surface is categorized as diffuse or specular. Specular reflection corresponds to the gloss while diffuse reflection defines the colour. The major portion of reflected light is as diffuse reflection with only about 4% as specular reflection. Specular included measurements measure the total amount of light reflected regardless of the state of the surface. Specular excluded measurement more closely corresponds to the assessment by a human observer.

Colour measurements with specular excluded were taken for the first set of experiments to investigate the potential influence of the scattering effect of superficial dye particles on the colour properties of the dyed samples. The L* values of all the dyed fabrics are higher with specular excluded indicating a lightening of the colour as illustrated in Tables 4.15 – 4.19. This is to be expected as the human observer tends to ignore the gloss component of the reflection and thus the colour would appear lighter. Also, the total amount of light reflected consists of both diffuse and specular reflection and when one of the components is excluded, the total amount of light reflected decreases. This change is minor for samples dyed with dyes **1**, **2** and **3**.

In the case of samples dyed with dye **1** (Tables 4.19 and 4.15), chroma has a higher value for specular included both before and after reduction clearing. However within each set of conditions, all the respective trends are same.

Table 4.15 Colour measurements of the samples dyed with dye **1** before and after reduction clearing with sodium dithionite with specular excluded

Shade		L*	a*	b*	C*	h°	Integ value
1 %	Untreated	83.42	8.94	104.43	104.82	85.11	21.83
	Reduction cleared	84.17	8.92	105.84	106.21	85.18	22.02
2 %	Untreated	80.84	14.27	104.3	105.27	82.21	26.04
	Reduction cleared	81.83	14.63	105.91	106.92	82.13	25.99
3 %	Untreated	78.73	17.72	102.1	103.62	80.15	27.12
	Reduction cleared	79.76	18.13	104.1	105.66	80.12	27.62
4%	Untreated	77.21	19.27	100.05	101.88	79.1	27.52
	Reduction cleared	78.37	19.78	102.28	104.18	79.05	28.04
5 %	Untreated	77.23	19.87	100.37	102.32	78.8	27.89
	Reduction cleared	78.24	20.52	102.18	104.22	78.64	28.08

In the case of samples dyed with dye **2** (Table 4.16), a specific trend could not be identified for chroma value with specular excluded.

Table 4.16 Colour measurements of the samples dyed with dye **2** before and after reduction clearing with sodium dithionite with specular excluded

Shade		L*	a*	b*	C*	h°	Integ value
1 %	Untreated	31.84	43.77	3.58	43.92	4.68	27.96
	Reduction cleared	32.3	45.05	3.53	45.19	4.48	27.53
2 %	Untreated	26.9	38.45	6.28	38.96	9.27	41.02
	Reduction cleared	27.05	39.97	6.27	40.46	8.92	41.65
3 %	Untreated	24.58	34.21	7.22	34.96	11.91	47.82
	Reduction cleared	24.5	34.95	6.84	35.61	11.07	48.48
4 %	Untreated	23.26	31.08	7.43	31.96	13.45	51.71
	Reduction cleared	23.33	31.77	6.81	32.49	12.1	51.19
5 %	Untreated	22.21	27.57	7.17	28.48	14.58	54.06
	Reduction cleared	22.09	28.73	6.41	29.44	12.58	54.62

Table 4.17 Colour measurements of samples dyed with dye **3** before and after reduction clearing with sodium dithionite with specular excluded

Shade		L*	a*	b*	C*	h°	Integ value
1 %	Untreated	30.63	44.41	7.34	45.02	9.39	33.62
	Reduction cleared	30.55	44.81	6.88	45.34	8.73	33.92
2 %	Untreated	25.75	37.11	8.74	38.13	13.26	46.51
	Reduction cleared	25.52	37.78	8.6	38.75	12.83	48.07
3 %	Untreated	23.5	32.28	8.52	33.38	14.79	52.74
	Reduction cleared	23.39	32.97	8.3	34	14.13	53.64
4 %	Untreated	22.2	28.39	7.81	29.44	15.39	55.56
	Reduction cleared	21.8	28.6	7.6	29.59	14.89	57.64
5 %	Untreated	21.16	24.52	7.2	25.55	16.36	57.77
	Reduction cleared	20.98	25.99	7.03	26.92	15.13	59.54

Table 4.18 Colour measurements of samples dyed with dye **4** before and after reduction clearing with sodium dithionite with specular excluded

Shade		L*	a*	b*	C*	h°	Integ value
1%	Untreated	33.49	-0.86	-35.83	35.84	268.63	19.75
	Reduction cleared	32.73	0.33	-36.68	36.68	270.51	20.98
2%	Untreated	25.86	4.02	-33.03	33.27	276.94	31.49
	Reduction cleared	26.57	4.05	-34.54	34.78	276.68	30.92
3%	Untreated	22.81	5.69	-30.51	31.04	280.57	37.47
	Reduction cleared	24.09	5.44	-32.56	33.01	279.48	35.37
4%	Untreated	20.42	6.73	-27.28	28.1	283.85	42.54
	Reduction cleared	20.9	6.79	-28.52	29.32	283.38	41.71
5%	Untreated	19.9	6.63	-24.56	25.44	285.11	42.54
	Reduction cleared	19.75	6.98	-26.61	27.51	284.71	44.56

For samples dyed with dye **3** (Tables 4.11 & 4.17) and dye **5** (Tables 4.13 & 4.19), chroma before reduction clearing measured with specular included and excluded gives almost identical values.

Table 4.19 Colour measurements of samples dyed with dye **5** before and after reduction clearing with sodium dithionite with specular excluded

Shade		L*	a*	b*	C*	h°	Integ value
1 %	Untreated	54.49	-19.5	-30.38	36.1	237.3	5.89
	Reduction cleared	55.4	-18.72	-33.81	38.64	241.03	5.78
2 %	Untreated	45.58	-16.22	-32.99	36.76	243.81	11.4
	Reduction cleared	46.38	-15.73	-35.03	38.4	245.81	11.12
3 %	Untreated	41.02	-13.64	-33.87	36.52	248.06	15.47
	Reduction cleared	41.2	-12.65	-35.08	37.29	250.17	15.28
4 %	Untreated	37.32	-10.77	-33.97	35.64	252.42	19.03
	Reduction cleared	37.38	-9.77	-35.25	36.58	254.51	19.02
5 %	Untreated	34.26	-7.86	-33.9	34.8	256.95	22.15
	Reduction cleared	34.33	-7.16	-34.97	35.69	258.43	22.32

The integ values of samples dyed with dye **5** are slightly lower when measurements are taken with specular excluded. The colour properties of samples dyed with dye **5** are not influenced to a significant degree by reduction clearing with sodium dithionite. Sampled dyed with dye **5** also gave an unusual response during washfastness tests as there was no staining of the multifibre fabric.

The integ values of all the dyed samples are higher when specular component is included. This change is more pronounced in the case of samples dyed with dye **3** (Table 4.114.11 & 4.17). Saturation or chroma of the dyed samples does not show much difference under both conditions. In view of the fact that the differences are small and do not provide evidence helpful for interpretation of the effect of reduction clearing, subsequent investigation used only specular included measurement.

4.4.6 Scanning Electron Microscopy after Reduction Clearing with Sodium Dithionite

The samples were subjected to scanning electron microscopy to observe the possibility of particles present on the fabric surface. A number of images at various magnifications were captured but only a selected few are included here. Micrographs in Figure 4.7 are the images for the undyed polyester fabric. These show a cleaner surface with only a small amount of some particles which may be dirt or some other impurity left from previous

treatment. The fibres also show slight damage which may be due to the pre-treatments. Micrographs of samples dyed with dyes **1**, **2, 3** and **4** before reduction clearing show significant number of extraneous particles which were not present on the undyed fibre (Figures 4.8, 4.10, 4.12 and 4.14). It seems reasonable to infer that these particles are either dye or oligomers. Many of the particles observed on the fibre surfaces have a polygonal structure. The micrographs of samples dyed with dye **5** (Figure 4.16) have a relatively lower number of superficial particles before reduction clearing. The images for the samples dyed with dyes **1**, **2**, **3** and **4** after reduction clearing show reduced numbers of particles when compared with the untreated samples. Fabric samples dyed with dyes **1** and **2** (Figure 4.9 & Figure 4.11) show significantly cleaner fibres after reduction clearing whereas samples dyed with dyes **3** and **4** (Figure 4.13 & Figure 4.15) show a smaller difference. These results are consistent qualitatively with the fastness and acetone extraction results whereby surface dye on samples dyed with dyes **3** and **4** appear to be less susceptible to removal by reduction clearing.

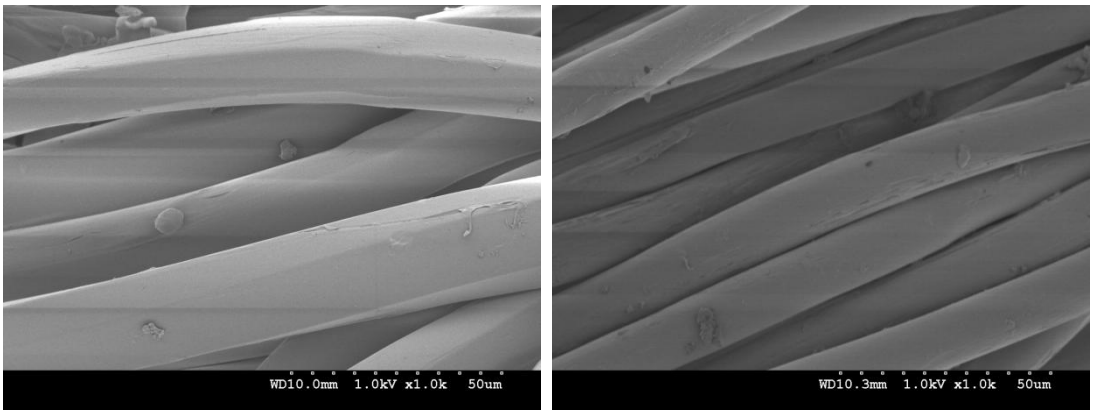


Figure 4.7 SEM images of undyed polyester

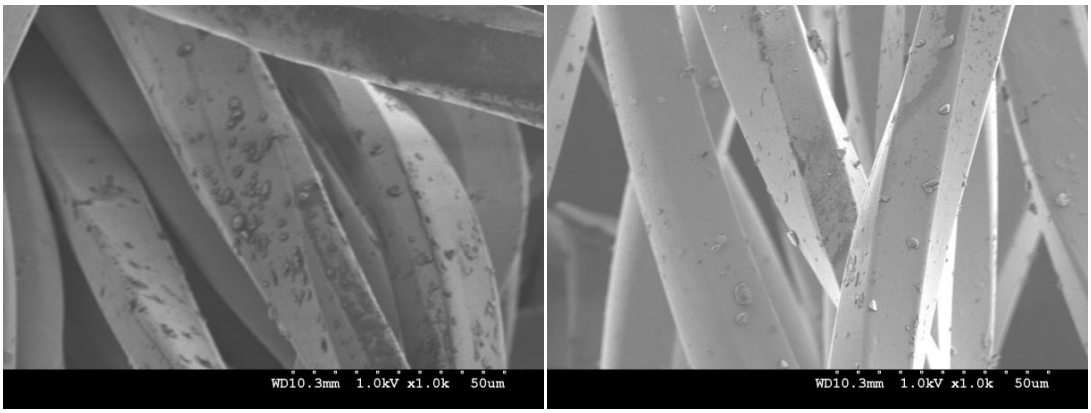


Figure 4.8 SEM images of samples dyed with dye **1** before reduction clearing

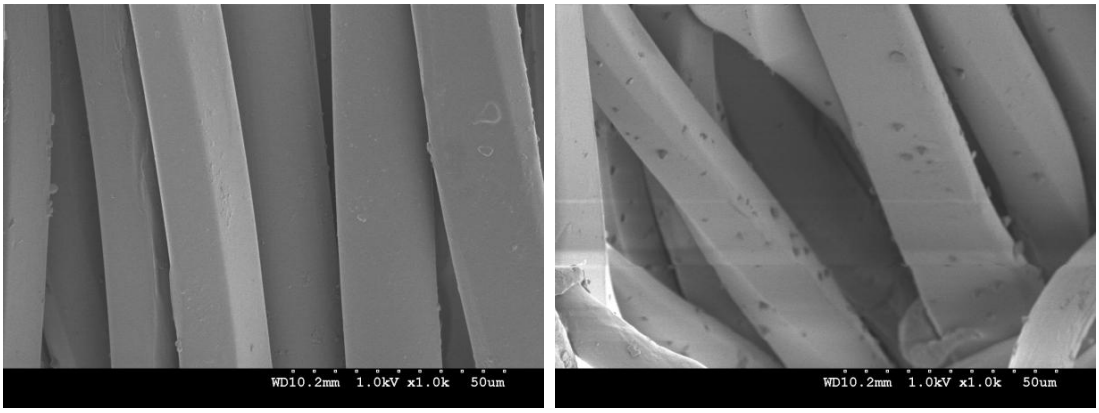


Figure 4.9 SEM images of samples dyed with dye **1** after reduction clearing

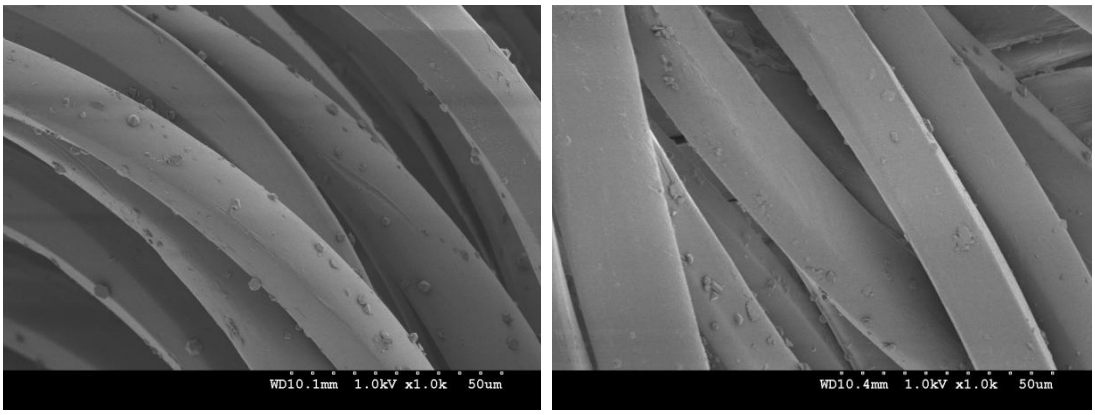


Figure 4.10 SEM images of samples dyed with dye **2** before reduction clearing

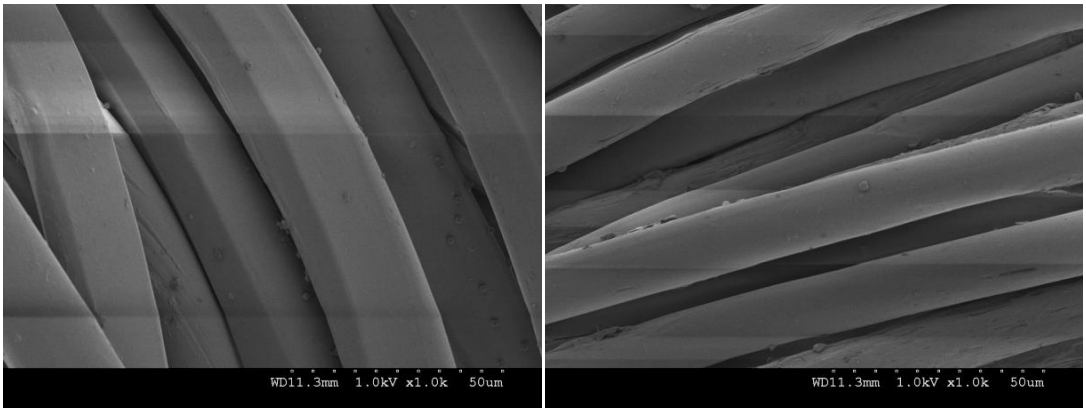


Figure 4.11 SEM images of samples dyed with dye **2** after reduction clearing

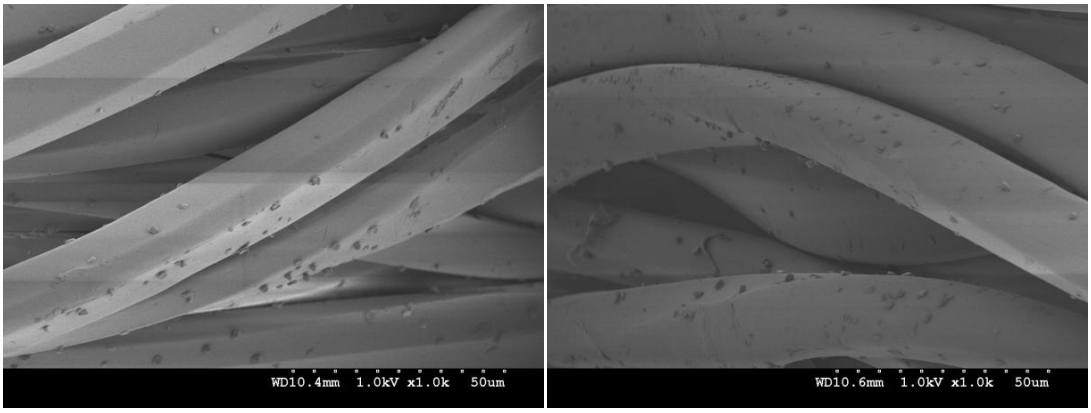


Figure 4.12 SEM images of samples dyed with dye **3** before reduction clearing

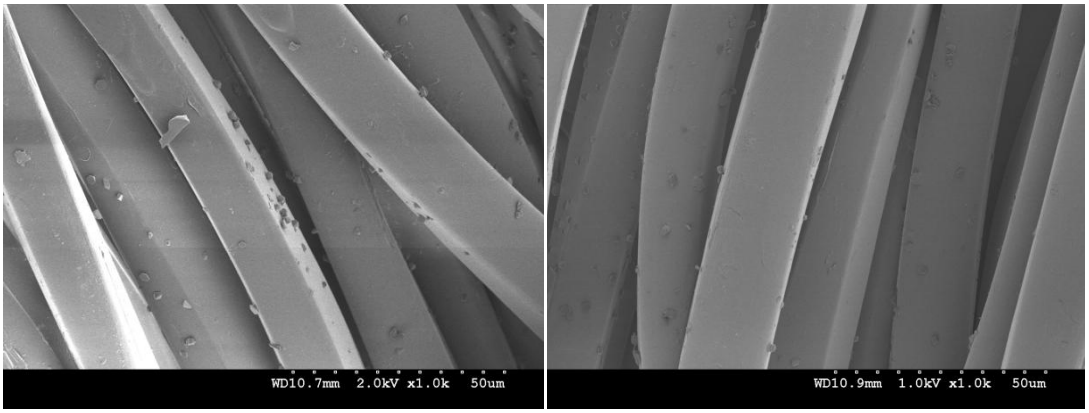


Figure 4.13 SEM images of samples dyed with dye **3** after reduction clearing

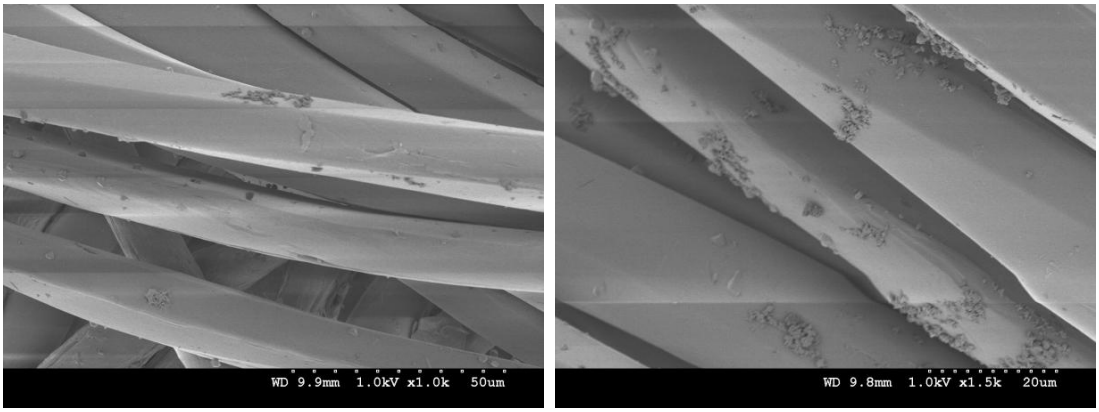


Figure 4.14 SEM images of samples dyed with dye **4** before reduction clearing

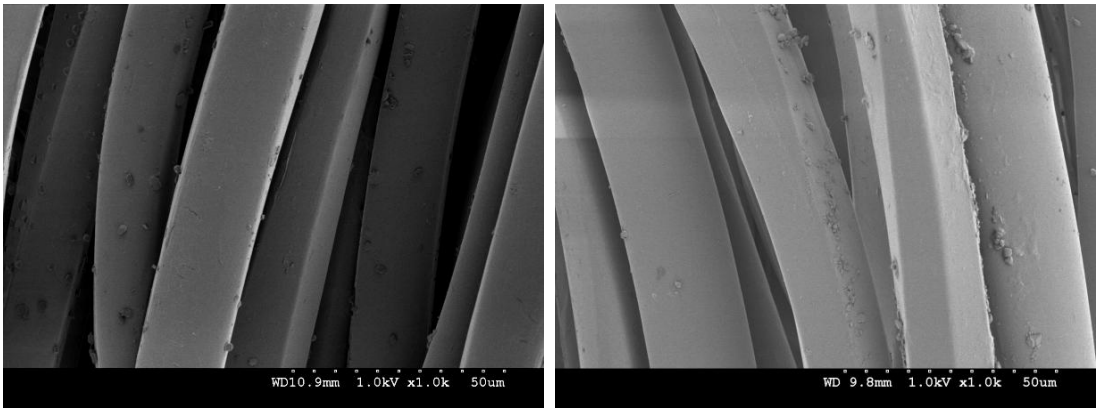


Figure 4.15 SEM images of samples dyed with dye **4** after reduction clearing

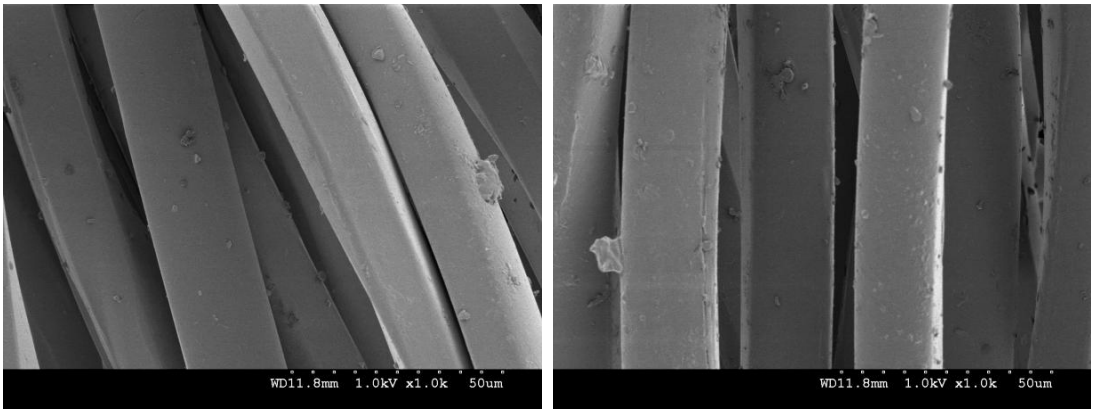


Figure 4.16 SEM images of samples dyed with dye **5** before reduction clearing

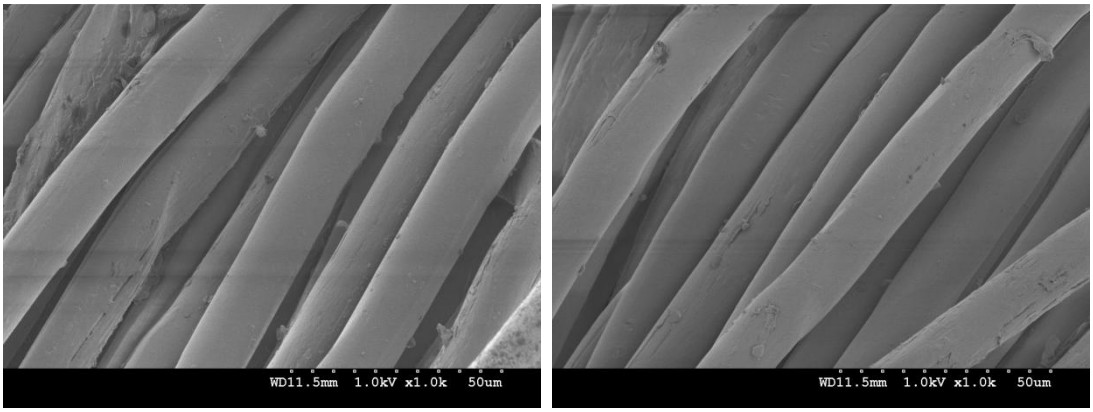


Figure 4.17 SEM images of samples dyed with dye **5** after reduction clearing

In the case of samples dyed with dye **4**, these particles do not have a well-defined structure and are clustered together. These images thus correlate well with the proposal made about higher tendency of dye **4** towards aggregation (Section 4.4.1). However, after reduction clearing the micrographs show a decrease in the amount of clusters but some polygonal structures can also be seen.

4.5 Reduction Clearing with Organic Reducing Agents

4.5.1 Reduction Clearing with Formamidine Sulphinic Acid and Hydroxyacetone

Reduction clearing with formamidine sulphinic acid/thiourea dioxide (FAS/TUDO) and hydroxyacetone was carried out following the same pattern of investigations as was used with sodium dithionite. The concentration of reducing agents and the application conditions which were used for reduction clearing with sodium dithionite were also used for FAS/TUDO and hydroxyacetone. Both FAS/TUDO and hydroxyacetone were applied under these conditions for the reduction clearing of all the five dyes at all five depths of shade. Reduction clearing with FAS/TUDO and hydroxyacetone was carried out to provide a comparison with sodium dithionite, and thus, optimisation experiments were not performed for these two organic reducing agents. Samples dyed with dye **3** were also reduction cleared with FAS/TUDO and hydroxyacetone at a lower concentration. Assessment of the effect of reduction clearing was carried out using the acetone extraction test, determination of the washfastness, rubfastness and by measuring the colour properties of the treated samples, as in the case of sodium dithionite. It was decided that the tests for fastness to perspiration were unnecessary as washfastness tests had provided a better indication of the clearing efficiency in the case of sodium dithionite. Treated samples were also subjected to scanning electron microscopy to examine the surface of the fabric. The results obtained are discussed in the following sections.

4.5.2 Assessment of Surface Dye Removal

The absorbance values and concentrations of the dyes in the acetone extracts obtained from the dyed samples after reduction clearing with FAS/TUDO and hydroxyacetone using the same concentration and conditions as were used for reduction clearing with sodium dithionite are given in Table 4.20.

As shown in Table 4.20, samples dyed with dye **1** give dye concentrations in the extract greater than 10 mg l^{-1} at 3, 4 and 5% depths of shade. Reduction clearing with FAS/TUDO and hydroxyacetone results in a significantly lower concentration of dye **1** in the acetone extract, less than 2 mg l^{-1}.

Table 4.20 Concentration of dyes in the acetone extract of dyed samples after reduction clearing with FAS/TUDO and hydroxyacetone (2.14 g l^{-1}, 70°C)

		Untreated			Reduction clearing with					
					FAS/TUDO			Hydroxyacetone		
	Shade %	λ_{max} (nm)	Abs.	Conc. (mg l^{-1})	λ_{max} (nm)	Abs.	Conc. (mg l^{-1})	λ_{max} (nm)	Abs.	Conc. (mg l^{-1})
Dye **1**	1	439	0.25	2.50	438	0.07	0.69	438	0.06	0.64
	2	439	0.55	5.52	438	0.09	0.90	438	0.11	1.07
	3	440	1.24	12.33	439	0.14	1.41	438	0.15	1.54
	4	440	1.58	15.81	438	0.14	1.41	438	0.14	1.39
	5	442	3.00	29.95	439	0.15	1.49	439	0.15	1.52
Dye **2**	1	511	0.42	5.02	508	0.04	0.52	509	0.03	0.39
	2	511	0.86	10.33	508	0.06	0.75	508	0.08	0.99
	3	510	1.86	22.43	509	0.11	1.28	509	0.08	0.92
	4	511	2.73	32.91	509	0.10	1.25	508	0.11	1.37
	5	511	5.49	66.24	510	0.24	2.90	509	0.24	2.93
Dye **3**	1	512	0.46	4.03	509	0.06	0.51	485	0.07	0.58
	2	512	1.17	10.25	510	0.07	0.64	491	0.10	0.87
	3	512	1.92	16.82	511	0.12	1.07	494	0.16	1.44
	4	511	3.59	31.46	511	0.27	2.33	495	0.28	2.46
	5	511	5.43	47.58	508	0.26	2.30	494	0.31	2.67
Dye **4**	1	666	0.09	1.95	666	0.02	0.33	621	0.02	0.51
	2	666	0.22	4.24	664	0.04	0.60	664	0.02	1.31
	3	666	0.36	7.92	665	0.05	1.26	664	0.04	3.63
	4	665	0.48	7.49	664	0.08	1.26	661	0.09	3.57
	5	666	0.88	11.39	664	0.11	2.06	661	0.09	5.333
Dye **5**	1	631	0.12	2.34	629	0.03	0.50	628	0.04	0.41
	2	630	0.26	5.38	629	0.05	0.94	630	0.10	0.61
	3	630	0.40	8.92	630	0.10	1.23	630	0.28	0.94
	4	630	0.63	11.96	630	0.10	1.99	629	0.28	2.29
	5	630	0.86	22.02	629	0.16	2.74	630	0.42	2.29

The efficiency of the surface dye removal was calculated as a percentage by equation 4.2:

$$\%\ surface\ dye\ removed = \frac{A_o - A_f}{A_o} \times 100 \qquad (4.2)$$

where A_o = absorbance of the acetone extract from the original untreated dyed sample;

A_f = absorbance of the acetone extract from the reduction cleared sample.

The percentage surface dye removed may be considered as a measure of the efficiency of the clearing process. A comparison of the percentage of surface dye removal using the three reducing agents, that is, sodium dithionite, FAS/TUDO and hydroxyacetone with the untreated samples is shown in Figures 4.18 – 4.22.

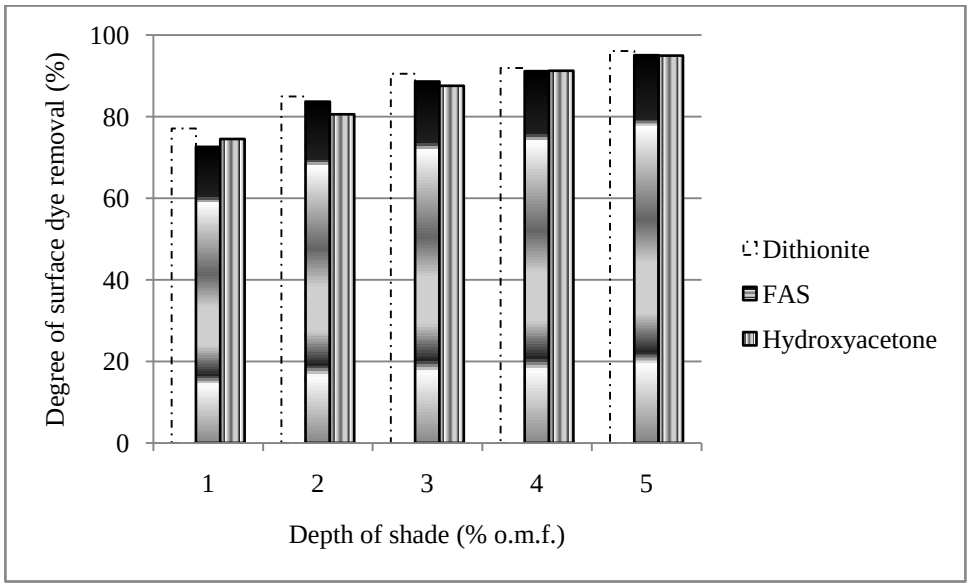


Figure 4.18 Degree of surface dye removal from the samples dyed with dye **1** after reduction clearing with sodium dithionite, FAS/TUDO and hydroxyacetone

A comparison of the degree of surface dye removal for samples dyed with dye **1**, expressed as a percentage after clearing with sodium dithionite, FAS/TUDO and hydroxyacetone is shown in Figure 4.18. It is observed that all three reducing agents are quite efficient in the removal of surface deposits of dye **1** giving a dye removal of 70 – 95%. However, sodium dithionite gives slightly better removal of unfixed surface dye than FAS/TUDO and hydroxyacetone while FAS/TUDO and hydroxyacetone show similar results especially at higher depths of shade. As is the case with sodium dithionite, FAS/TUDO and hydroxyacetone provide a higher degree of surface dye removal with increasing depth of

shade. A possible explanation for this behaviour which appeared unexpected at first sight is that there may be a certain amount of dye which is occluded or aggregated in such a way that it is not removed by the reduction clearing process but is removed by acetone extraction, the level of which, relative to the amount of accessible surface dye, increases with dye concentration. Another possibility may be that as the depth of shade increases, the amount of surface dye which is only loosely attached with the fibre also increases. Thus, this leads to an increase in the percentage of surface dye removed at higher depths of shade.

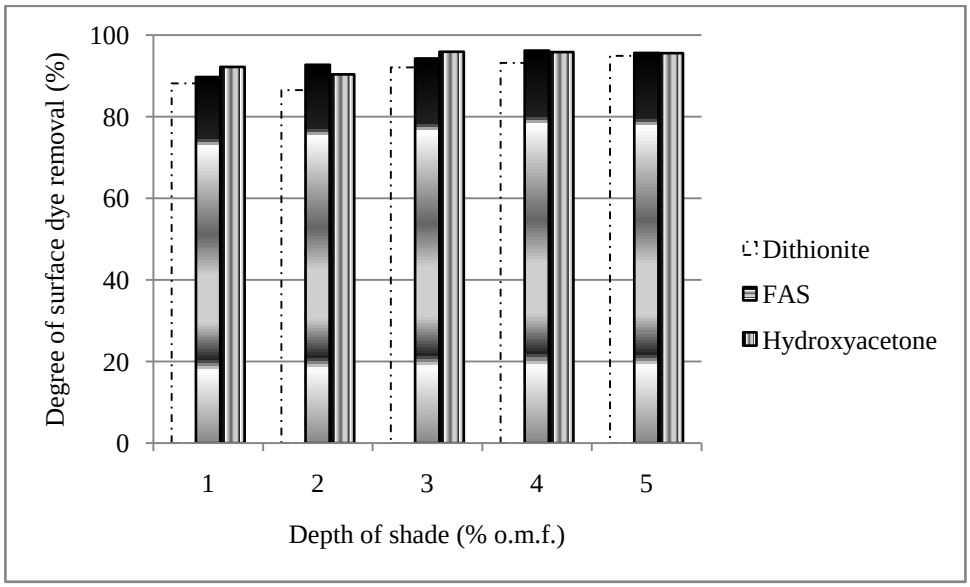


Figure 4.19 Degree of surface dye removal from the samples dyed with dye **2** after clearing with sodium dithionite, FAS/TUDO and hydroxyacetone

In the case of samples dyed with dye **2**, all three reducing agents are fairly efficient giving a dye removal of 80 – 95%. FAS/TUDO and hydroxyacetone remove slightly more surface dye as compared to sodium dithionite as shown in Figure 4.19. However, the difference between the efficiency of the three reducing agents decreases at higher depths of shade becoming almost the same at the 5% depth of shade (Figure 4.19). All three reducing agents are successful in removing deposits of surface dye resulting in a significant decrease in the concentration of dye **2** in the acetone extract as shown by the data given in Table 4.20. The percentage of surface dye removal from polyester dyed with dye **3** again broadly increases with increasing depth of shade (Figure 4.20). This increase is more pronounced in the case of reduction clearing with sodium dithionite than FAS/TUDO and hydroxyacetone. The organic reducing agents are the most efficient in this case also, giving surface dye

removal in the range 85-95%, with FAS/TUDO marginally better than hydroxyacetone. Reduction clearing with sodium dithionite is much less effective at removing this dye, giving surface dye removal in the range 20-55%. It may be proposed that the contrast between the structurally-similar dyes **2** and **3** towards reduction clearing with sodium dithionite as indicated by the percentage of dye removed may be attributable to the presence of acetyl groups in dye **2** which render it potentially susceptible to hydrolysis.

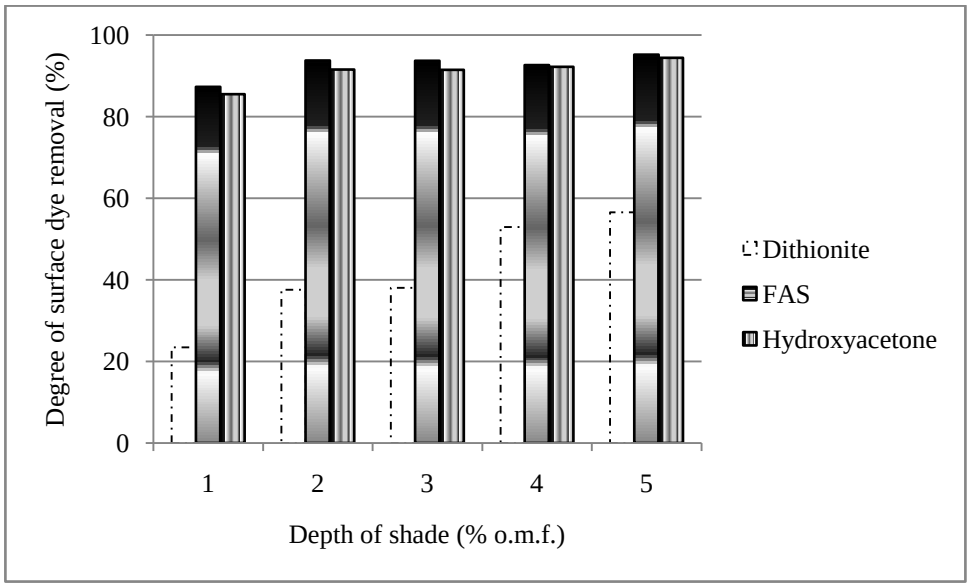


Figure 4.20 Degree of surface dye removal from the samples dyed with dye **3** after clearing with sodium dithionite, FAS/TUDO and hydroxyacetone

However, the organic reducing agents are nearly as efficient at removing dye **3** as dye **2**. Thus, dye **3** appears to be much more susceptible to reduction at the fibre surface by the organic reducing agents, than by the inorganic agent, sodium dithionite. It is likely that the mechanism of reduction with sodium dithionite is quite different to that with FAS/TUDO and hydroxyacetone. Interestingly, it appears that the two organic reducing agents, hydroxyacetone and FAS/TUDO, show similar behaviour in these cases, even though the details of the chemistry of the reduction mechanism are not the same, as outlined in Section 0. These results contrast, to a certain extent, with some literature reports which suggest a similarity between clearing with FAS/TUDO and sodium dithionite, which is not observed in the case of dye **3** at least in this study. The similarity between FAS/TUDO and sodium dithionite is possibly suggested because of their relatively similar redox potential values

(FAS/TUDO -1100 mV, sodium dithionite -970 mV) as compared with hydroxyacetone which has significantly lower reduction potential (-810 mV) [14].

Samples dyed with dye **4** give a lower concentration of dye in the acetone extract than samples dyed with dyes **1**, **2** and **3** (Table 4.20) with the highest concentration falling below 12 mg l^{-1} as compared with values of 30 – 67 mg l^{-1} for dyes **1**, **2** and **3**. A lower concentration of dye in the acetone extract indicates a higher degree of surface dye removal by reduction clearing. However, the effect of the three reducing agents varies widely in the case of surface dye removal from samples dyed with dye **4** (Figure 4.21).

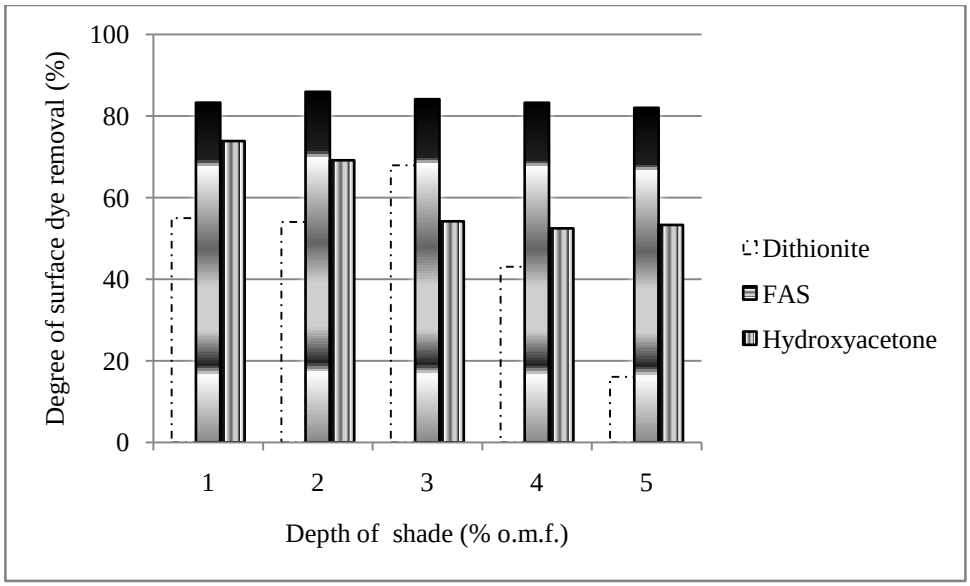


Figure 4.21 Degree of surface dye removal from samples dyed with dye **4** after clearing with sodium dithionite, FAS/TUDO and hydroxyacetone

As with dye **3**, the organic reducing agents provide highest efficiency, with sodium dithionite only removing about 65% surface dye at a maximum. Dye **4** is the only one of those studied where there is a significant difference in the clearing ability of the two organic reducing agents, FAS/TUDO and hydroxyacetone. FAS/TUDO is consistently more efficient giving surface dye removal above 80% at all depths of shade. Hydroxyacetone is rather less efficient, although better than sodium dithionite, except at the 3% depth of shade. This particular dye is likely to be relatively resistant to reduction as its molecular structure contains four electron releasing groups (NH_2 and OH) increasing the electron density in the anthraquinone ring system, and thus appears to require the superior reducing power of FAS/TUDO for efficient removal. Fabrics dyed with dye **4** provide a contrast with the other

dyes in that the percentage of surface dye removed by reduction clearing decreases with increasing depths of shade. This decrease is quite regular and significant after reduction clearing with sodium dithionite and hydroxyacetone whereas FAS/TUDO only shows a minor change in the percentage of surface dye removal in the case of samples dyed with dye **4** as the depth of shade is varied. The possibility has been proposed in Section 4.4 that this particular dye becomes so increasingly aggregated at the surface as the depth of shade increases that it becomes progressively more difficult to remove [4].

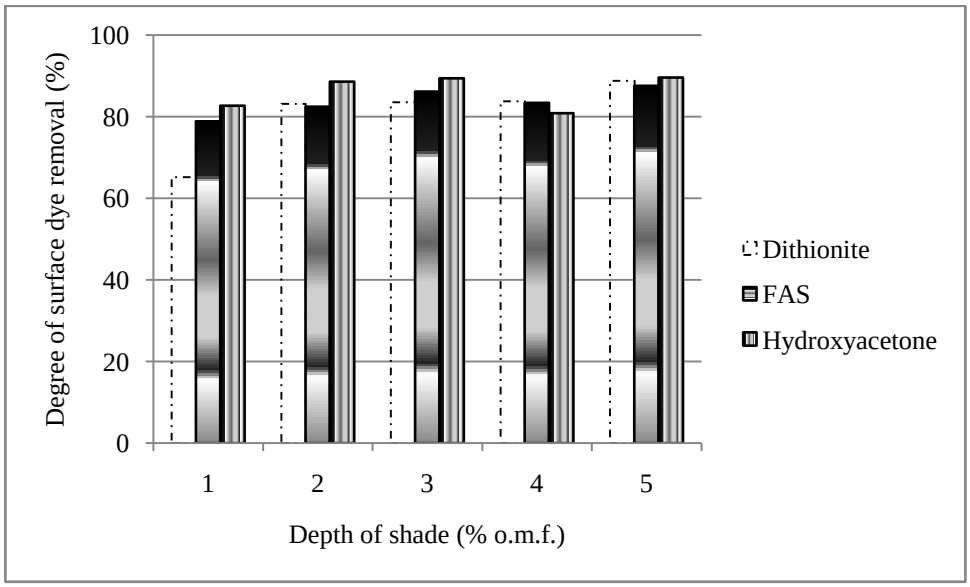


Figure 4.22 Degree of surface dye removal from the samples dyed with dye **5** after clearing with sodium dithionite, FAS/TUDO and hydroxyacetone

Similar to dye **4**, samples dyed with dye **5** have a lower amount of dye present on the surface as indicated by the concentration of dye in the acetone extract (Table 4.20) when compared with the three azo dyes, **1**, **2** and **3**. However, the concentration of dye **5** in the acetone extract is higher than the concentration of dye **4** in the acetone extract. The efficiency of reduction clearing on polyester dyed with dye **5** is around 80-90% and the three reducing agents are equally good in the clearing of the surface with no clear differentiation between the three reducing agents (Figure 4.22), except at the 1% depth of shade where sodium dithionite is less effective.

The above results indicate that FAS/TUDO and hydroxyacetone are slightly better than or at least equally as good as sodium dithionite in the removal of surface dye from the dyed samples when used under the same conditions. FAS/TUDO is significantly more effective

clearing agent than sodium dithionite in the case of samples dyed with dyes **3** and **4** at all depths of shade while for samples dyed with dyes **1**, **2** and **5** FAS/TUDO gives comparable efficiency to that of sodium dithionite as indicated by the percentage of surface dye removed. In the case of samples dyed with dye **3**, the difference between the percentage of surface dye removed after reduction clearing with sodium dithionite and FAS/TUDO decreases as the depth of shade increases. However, in the case of samples dyed with dye **4** the difference between the efficiency of sodium dithionite and FAS/TUDO increases at higher depths of shade. Hydroxyacetone also shows a similar trend to FAS/TUDO concerning the percentage of surface dye removal. This is an interesting observation as previous reports, as discussed in Section 0, suggest that FAS/TUDO is more efficient than sodium dithionite while hydroxyacetone is less efficient even when applied at 100°C [11]. The higher reducing efficiency of FAS/TUDO may be attributed to its higher negative redox potential than sodium dithionite. To investigate the possibility of using a reduced quantity of FAS/TUDO and hydroxyacetone, selected experiments of reduction clearing were carried out, both with FAS/TUDO and with hydroxyacetone, at a concentration 4 times lower than that originally used, but at the same temperature (70°C) and for the same time (20 min). The investigation was restricted to fabrics dyed with dye **3** on the basis that it has consistently provided good discrimination in the evaluation of washfastness properties, especially as indicated by staining on nylon.

Table 4.21 Concentration of dye **3** in acetone extract of samples dyed with dye **3** after reduction clearing with FAS/TUDO and hydroxyacetone

Depth of shade (%)	FAS/TUDO (g l^{-1})						Hydroxyacetone (g l^{-1})					
	2.14			0.54			2.14			0.54		
	λ_{max} (nm)	Abs.	Conc. (mg l^{-1})	λ_{max} (nm)	Abs.	Conc. (mg l^{-1})	λ_{max} (nm)	Abs.	Conc. (mg l^{-1})	λ_{max} (nm)	Abs.	Conc. (mg l^{-1})
1	509	0.06	0.51	504	0.17	1.53	485	0.07	0.58	466	0.09	0.76
2	510	0.07	0.64	504	0.52	4.59	491	0.10	0.87	475	0.23	1.98
3	511	0.12	1.07	495	0.76	6.67	494	0.16	1.44	475	0.37	3.28
4	511	0.27	2.33	493	0.98	8.57	495	0.28	2.46	479	0.48	4.22
5	508	0.26	2.30	489	1.54	13.52	494	0.30	2.67	477	0.75	6.61

The comparison of the amount of surface dye removed from samples dyed with dye **3** after reduction clearing with the two concentrations of FAS/TUDO and hydroxyacetone is given in Figure 4.23 and the data is presented in Table 4.21. Both of the organic reducing agents remove a higher percentage of surface dye even when used at a lower concentration than after reduction clearing with sodium dithionite at a higher concentration, which gives only 20 – 60% dye removal. FAS/TUDO and hydroxyacetone, when used at a higher concentration, give a significantly lower concentration of dye in the acetone extract. This indicates that the fibre surface is exceptionally clean.

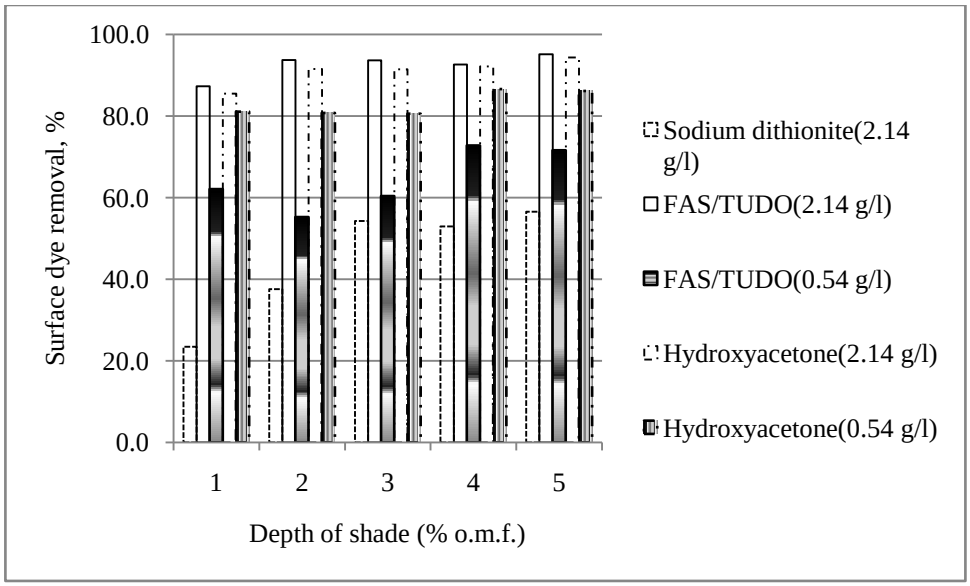


Figure 4.23 Degree of surface dye removal after reduction clearing of samples dyed with dye **3** with FAS/TUDO and hydroxyacetone

Another interesting feature which can be observed from Figure 4.23 is that at a lower concentration, hydroxyacetone is better at the removal of surface dye than FAS/TUDO as it removes about 80% surface dye as compared to 55 – 75% of surface dye removed by FAS/TUDO. At a higher concentration, FAS/TUDO performs slightly better than hydroxyacetone in the removal of superficial dye, although, this difference between the efficiency of the two organic reducing agents decreases at higher depth of shades. The efficiency of hydroxyacetone is affected to a lesser extent with a decrease in concentration, only decreasing by about 10% at the most. This feature is in line with previous studies which report that the redox potential of hydroxyacetone is relatively stable and does not

change significantly with an increase in its concentration [95]. In contrast, the efficiency of FAS/TUDO decreases by as much as 40% on decreasing its concentration.

At lower concentrations of both FAS/TUDO and hydroxyacetone, the wavelength of the maximum absorption in the acetone extract shifts to lower values that is, a hypsochromic shift is observed (Table 4.21), which is anomalous compared with sodium dithionite. This shift in wavelength, in the case of FAS/TUDO, increases with an increase in depth of shade while the change produced in the case of hydroxyacetone is almost constant for all the five depths of shade. The change in wavelength of the absorption maxima suggests that the acetone extract may contain some coloured species different from the parent dye. These differently coloured species may be the result either of degradation of dye or of oxidation of the reducing agent. It has been reported that hydroxyacetone transforms into various products on oxidation in alkaline medium. Although most of them having unconfirmed identities, the presence of enediol structures is reported. These oxidative degradation products are proposed as the cause of odour under dyeing conditions [93, 209]. However, there is no comparable report of FAS/TUDO producing any such products. Thus, the change in wavelength of absorption maxima may be attributed to the presence of the products of dye degradation which in the case of hydroxyacetone may be due to either the degradation products from the dye or oxidation products of hydroxyacetone. The interpretation of the absorbance/concentration values in acetone extracts where the wavelength is changed should be carried out with some caution. It is noted that such a shift in absorption maxima was not observed after reduction clearing with sodium dithionite (Table 4.2).

It is suggested in previous literature concerning the reduction clearing of disperse dyed polyester that FAS/TUDO may perform at a similar level to that of sodium dithionite even when used at a significantly lower concentration compared with the latter [11]. However, in this investigation this generalization is found to be valid only in the case of samples dyed with dye **3** and for samples dyed with dye **4** at higher depths of shade, as indicated by the results of acetone extraction of the dyed samples after treatment with FAS/TUDO.

4.5.3 Washfastness Properties after Reduction Clearing with FAS/TUDO and Hydroxyacetone

The washfastness properties after reduction clearing with FAS/TUDO and hydroxyacetone of the samples dyed with the selected five dyes at the range of concentrations are given in Table 4.22. Both the organic reducing agents, FAS/TUDO and hydroxyacetone generally improve the fastness to ratings of 4-5 or 5. There is no significant difference in the washfastness properties of the samples reduction cleared with FAS/TUDO and hydroxyacetone. The only exception is seen for samples dyed with dye **4,** in which case FAS/TUDO performs better than hydroxyacetone in improving the washfastness properties as indicated by stain ratings.

The two dyes which generally responded poorly to reduction clearing with sodium dithionite are dyes **3** and **4** (Table 4.5)**.** Both FAS/TUDO and hydroxyacetone are better than sodium dithionite in improving the washfastness properties of samples dyed with dye **3** while only FAS/TUDO provides better results than sodium dithionite in the case of samples dyed with dye **4.** These results are thus consistent with the measured level of surface dye removal as illustrated in Figures 4.18-4.22. There is thus a strong qualitative correlation throughout between the assessments of washfastness and surface dye removal. An unusual trend is observed in the case of samples dyed with dye **5** after reduction clearing with hydroxyacetone. There is a slight decrease in the stain ratings on nylon at higher depths of shade of samples dyed with dye **5**. It has been previously demonstrated in Section 4.4 that dye **5** is not particularly suitable for the evaluation of reduction clearing as it does not provide useful discrimination with respect to washfastness. In the case of clearing of samples dyed with this high energy dye with sodium dithionite, there was no staining of any of the component white fibres of the multifibre fabric during the test either before or after the clearing processes. It has been proposed that any surface dye removed during the washing test is not taken up by the white fabrics under the test conditions used. However, there is marginal staining of nylon after reduction clearing of samples dyed with dye **5** with hydroxyacetone, and the staining is a yellow colour, suggesting that the products formed on the reduction of dye with hydroxyacetone have a tendency for staining.

Table 4.22 Washfastness properties of the dyed samples after reduction clearing with FAS/TUDO and hydroxyacetone (HA) (2.14 g l^{-1}, 70°C)

		Shade (%)	Change in colour	Staining					
				Wool	Acrylic	PET	Nylon	Cotton	Acetate
Dye **1**	Reduction cleared with FAS / TUDO	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5
	Reduction cleared with HA	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	5	5	5
		4	5	5	5	5	5	5	5
		5	5	5	5	5	5	5	5
Dye **2**	Reduction cleared with FAS / TUDO	1	4-5	5	5	5	5	5	5
		2	4-5	5	5	5	5	5	4-5
		3	4-5	5	5	5	5	5	4-5
		4	4-5	5	5	5	5	5	4-5
		5	4-5	5	5	5	4-5	5	4-5
	Reduction cleared with HA	1	5	5	5	5	5	5	5
		2	4-5	5	5	5	5	5	5
		3	4-5	5	5	5	5	5	5
		4	4-5	5	5	5	5	5	4-5
		5	4-5	5	5	5	5	5	4-5
Dye **3**	Reduction cleared with FAS / TUDO	1	5	5	5	5	5	5	5
		2	5	5	5	5	4-5	5	4-5
		3	5	5	5	5	4-5	5	4-5
		4	5	5	5	5	4-5	5	4
		5	5	5	5	4-5	4	5	4
	Reduction cleared with HA	1	5	5	5	5	5	5	5
		2	5	5	5	5	4-5	5	4-5
		3	5	5	5	5	4-5	5	4-5
		4	5	5	5	4-5	4	5	4
		5	5	5	5	4-5	4	5	4

		Shade (%)	Change in colour	Staining					
				Wool	Acrylic	PET	Nylon	Cotton	Acetate
Dye **4**	Reduction cleared with FAS / TUDO	1	4-5	5	5	5	5	5	5
		2	4-5	5	5	5	4-5	5	5
		3	4-5	5	5	5	4-5	5	4-5
		4	4-5	5	5	5	4	5	5
		5	4-5	5	5	5	4	5	4-5
	Reduction cleared with HA	1	5	5	5	5	4-5	5	5
		2	5	5	5	4-5	4	5	4-5
		3	5	4-5	5	4-5	3-4	4-5	4
		4	5	4-5	5	4-5	3-4	4-5	4
		5	5	4-5	5	4-5	3	4-5	4
Dye **5**	Reduction cleared with FAS / TUDO	1	4-5	5	5	5	5	5	5
		2	4-5	5	5	5	5	5	5
		3	4-5	5	5	5	5	5	5
		4	4-5	5	5	5	5	5	5
		5	4-5	5	5	5	5	5	5
	Reduction cleared with HA	1	5	5	5	5	5	5	5
		2	5	5	5	5	5	5	5
		3	5	5	5	5	4-5	5	5
		4	5	5	5	5	4-5	5	5
		5	5	5	5	5	4-5	5	5

The washfastness results for the samples cleared with the two organic reducing agents, FAS/TUDO and hydroxyacetone at the lower concentration are given in Table 4.23. Comparison with the corresponding data given in Table 4.22 or the clearing at the higher concentration confirms the deterioration in efficiency of dye removal in all cases. The results also confirm that FAS/TUDO is less efficient as a clearing agent than hydroxyacetone at the lower concentration. Hydroxyacetone is effective in reduction clearing at the lowest depth of shade giving washfastness ratings of 4-5 or 5, but its performance deteriorates progressively with increasing depth of shade. Hydroxyacetone gives quite high percentage of surface dye removal, about 80%, when used at lower concentration for the reduction clearing of samples dyed with dye **3** (Figure 4.23). However, despite removing a significant amount of surface dye, hydroxyacetone fails to

provide meaningful improvement in the washfastness properties of samples dyed with dye **3** at higher depths of shade.

Table 4.23 Washfastness properties of samples dyed with dye **3** (3% o.m.f.) after reduction clearing with FAS/TUDO and hydroxyacetone (HA) (0.54 g l^{-1}, 70°C)

		Shade (%)	Change in colour	Staining					
				Wool	Acrylic	PET	Nylon	Cotton	Acetate
Dye **3**	Reduction cleared with FAS/ TUDO	1	4-5	5	5	4-5	4	5	4
		2	4-5	4-5	5	4-5	3	4-5	3
		3	4-5	4	4-5	4	2-3	4-5	2-3
		4	5	4	4-5	3-4	2	4-5	2
		5	5	3-4	4-5	3-4	1-2	4-5	1-2
	Reduction cleared with HA	1	4-5	5	5	5	4-5	5	4-5
		2	4-5	4-5	5	5	4	5	4
		3	5	4-5	5	5	3	5	3
		4	5	4-5	5	4-5	2-3	5	2-3
		5	5	4-5	5	4-5	2	5	2

4.5.4 Rubfastness Properties after Reduction Clearing with FAS/TUDO and Hydroxyacetone

Rubfastness properties of all the samples after reduction clearing with FAS/TUDO and hydroxyacetone when used at the same concentration as sodium dithionite is excellent as shown in Table 4.24. Reduction clearing with sodium dithionite also improved the rubfastness properties to excellent (Table 4.6), despite giving a lower percentage of dye removal than FAS/TUDO and hydroxyacetone. This indicates that this application feature is rather less sensitive to the presence of surface dye, at least in the cases investigated.

Table 4.24 Rubfastness properties of the dyed samples after reduction clearing with FAS/TUDO and hydroxyacetone (2.14 g l^{-1}, 70°C)

	Shade (%)	Dye **1**		Dye **2**		Dye **3**		Dye **4**		Dye **5**	
		Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Reduction clearing with FAS/TUDO	1	5	5	5	5	5	5	5	5	5	5
	2	5	5	5	5	5	5	5	5	5	5
	3	5	5	5	5	5	5	5	5	5	5
	4	5	5	4-5	5	5	5	5	5	5	5
	5	5	5	4-5	5	5	5	4-5	5	5	5
Reduction clearing with hydroxyacetone	1	5	5	4-5	5	5	5	5	5	5	5
	2	4-5	5	4-5	5	5	5	5	5	5	5
	3	4-5	5	4-5	5	5	5	5	5	5	5
	4	5	5	4-5	5	5	5	5	5	5	5
	5	5	5	4-5	5	5	5	4-5	5	5	5

Rubfastness of the samples dyed with dye **3** after reduction clearing with lower concentrations of FAS/TUDO and hydroxyacetone is given in Table 4.25.

Table 4.25 Rubfastness properties of samples dyed with dye **3** (3% o.m.f.) after reduction clearing with FAS/TUDO and hydroxyacetone (0.54 g l^{-1}, 70°C)

	FAS/TUDO					Hydroxyacetone				
Shade (%)	1	2	3	4	5	1	2	3	4	5
Dry	5	4-5	4-5	4-5	4	5	4-5	5	4-5	4-5
Wet	5	5	4-5	5	4-5	5	5	5	5	5

Similar to the washfastness results, rubfastness properties are also decreased at lower concentration of reducing agents. However, hydroxyacetone improves the rubfastness properties to a marginally higher degree than FAS/TUDO, when both are used at lower concentrations.

4.5.5 Colour Properties after Reduction Clearing with FAS/TUDO and Hydroxyacetone

Colour measurements of the samples dyed with the selected five dyes before and after reduction clearing with FAS/TUDO and hydroxyacetone are given in Appendix (Table 1 – Table 5). The differences in colour parameters before and after reduction clearing with TUDO/FAS are given in Table 4.26. In many cases, the data in Table 4.26 fail to show consistent trends, possibly due to the complexity of the phenomena affecting colour that are associated with the removal of surface dye, conceivably involving opposing effects, and also due to the rather small numerical values involved. The obvious statement may be made that the colour properties of the cleared fabric are determined not by the dye that is removed from the surface but by the dye which remains within the fabric. The effect on colour of the removal of other surface impurities, such as oligomers, which is outside the scope of the present study, is also unpredictable.

Nevertheless, trends may be detected in specific cases. Of particular interest are the overall colour difference values, most of which are significant, expressed in Table 4.26, as ΔE values derived from the CMC equation. In the case of samples dyed with azo dyes **1**-**3**, reduction clearing with sodium dithionite led to ΔE values which broadly increased with increasing depth of shade (Table 4.14). With FAS/TUDO, this trend is distinct for samples dyed with dye **3**. However, with dyes **1** and **2**, the trend is less clear although the largest difference is observed at either the 4% or 5% depth of shade. The behaviour of the samples dyed with the two blue anthraquinone dyes, **4** and **5**, is different. In the case of samples dyed with dye **4**, virtually identical colour differences are observed at all depths of shade while with dye **5** the colour differences decrease steadily with increasing depth of shade. Similar trends were also observed with these two dyes in the case of reduction clearing with sodium dithionite.

In terms of lightness, as represented by ΔL*, there is no consistent trend across the series of dyes, nor with depth of shade. The most notable ΔL* values are observed in fabrics dyed with dyes **1** and **5** which produces consistently lighter colours (positive ΔL* values). The effect on lightness in the case of dyes **2** and **3** is generally small, while with dye **4** the ΔL* values are insignificant at all depths of shade.

Table 4.26 Differences in colour parameters of the dyed samples after treatment with FAS/TUDO

	Shade (%)	ΔL*	Δa*	Δb*	ΔC*	ΔH*	ΔE (CMC)	Change in integ value
Dye **1**	1	0.07	-0.12	-1.05	-1.06	0.03	0.31	-1.16
	2	-0.09	0.71	-0.14	-0.04	-0.72	0.38	0.2
	3	0.82	0.45	2.3	2.35	-0.05	0.75	1.54
	4	1.93	-0.06	3.9	3.82	0.79	1.4	1.41
	5	1.3	-0.53	2.18	2.04	0.94	0.93	0.39
Dye **2**	1	-0.06	1.38	0.57	1.43	0.45	0.65	1.28
	2	0.86	2.19	-0.15	2.14	-0.5	1.15	-1.56
	3	-0.91	-0.07	0.14	-0.04	0.15	0.66	4.5
	4	-0.31	0.92	-0.29	0.83	-0.49	0.6	1.96
	5	-0.09	2.56	-0.47	2.38	-1.05	1.5	1.85
Dye **3**	1	0.55	0.83	0.39	0.88	0.25	0.52	-0.77
	2	0.03	1.05	-0.16	0.99	-0.39	0.52	0.63
	3	0.02	1.03	-0.3	0.93	-0.54	0.6	0.35
	4	0.17	2.56	-0.03	2.47	-0.67	1.36	1.03
	5	-0.85	1.12	-1.11	0.79	-1.36	1.43	4.17
Dye **4**	1	-0.08	0.5	-0.65	0.65	0.51	0.48	0.26
	2	0.04	0.12	-1.1	1.1	-0.04	0.52	1.06
	3	0.13	-0.1	-0.74	0.7	-0.26	0.43	0.4
	4	-0.11	0.06	-0.73	0.72	-0.12	0.4	1.14
	5	0.12	-0.13	-0.81	0.75	-0.34	0.52	0.32
Dye **5**	1	0.72	0.41	-2.63	2.04	1.71	1.48	-0.09
	2	1.44	-0.22	-1.54	1.49	0.46	1.01	-0.8
	3	1.15	0.06	-1.24	1.14	0.5	0.85	-0.97
	4	0.5	0.48	-1.37	1.17	0.85	0.84	-0.3
	5	0.22	0.58	-1.02	0.88	0.73	0.67	-0.06

It is generally acknowledged industrially that the main visual colouristic outcome of traditional reduction clearing is a brightening of the colour. It seems reasonable that surface dye in an aggregated form and with little molecular interaction with the fibre might lead to a dulling of the colour, so that its removal would brighten the colour. The colour parameter most likely to reflect a change in brightness is chroma (C*), a measure of saturation or 'colourfulness'. It is notable therefore that, with only a few exceptions, the samples show increased chroma after reduction clearing with FAS/TUDO, indicated by positive values of ΔC*, most of significant magnitude. With azo dyes **1**-**3**, and for anthraquinone dye **4**, there are significant increases in chroma although no distinct relationship with depth of shade. Samples dyed with dye **5** show higher chroma after reduction clearing, and the ΔC* values decrease consistently with the depth of shade. Integ values have been proposed as a measure of the visual depth or strength of colour. In the case of azo dyes **1**-**3**, most integ values increase after clearing with FAS/TUDO, implying increased colour strength, while the value decreases in a few cases at lower depths of shade. Larger increases are generally observed at higher depths of shade, although the relationships are not consistent. In the case of samples dyed with dye **4**, colour strength increases at all depths of shade but with no distinct trend. Dye **5** is unique in that the integ values decrease at all depths of shade after reduction clearing, although the change is small. The effect on hue as a result of clearing with FAS/TUDO is generally quite small, as indicated by the magnitude of ΔH* values, and also Δa* and Δb* values taking account of the particular colour of the dye in each case. In the case of azo dyes **1-3**, the most significant hue differences are observed at higher depths of shade (4 - 5%). At these depths of shade, the hue of samples dyed with yellow dye **1** becomes slightly greener (positive ΔH*, negative Δa*) while red dyes **2** and **3** become progressively bluer (negative ΔH*, negative Δb*). With blue dye **4**, the hue differences are not significant, while with dye **5** clearing causes a hue shift towards red. It is of interest to note the similarity of all of the colouristic trends due to reduction clearing with FAS/TUDO to those that have been previously reported using sodium dithionite in Section 4.4.5. Thus, a tentative correlation with the chemical class of the dye may be proposed which is that the colour properties of anthraquinone dyes are influenced to a relatively less degree than the azo dye.

The differences in colour parameters after reduction clearing with hydroxyacetone are given in Table 4.27.

Table 4.27 Differences in colour parameters after reduction clearing with hydroxyacetone

	Shade (%)	ΔL*	Δa*	Δb*	ΔC*	ΔH*	ΔE (CMC)	Change in integ value
Dye **1**	1	-0.2	-0.05	-1.4	-1.4	-0.07	0.41	-1.09
	2	-0.05	0.81	0.24	0.35	-0.77	0.42	0.74
	3	1.05	0.74	2.76	2.85	-0.25	0.92	1.67
	4	1.94	-0.1	4.11	4.02	0.86	1.46	1.77
	5	1.38	-0.48	2.62	2.48	0.98	1.04	0.95
Dye **2**	1	-0.01	1.38	0.61	1.43	0.48	0.66	1.16
	2	0.81	2.34	-0.1	2.29	-0.47	1.18	-1.18
	3	-0.76	-0.1	0.07	-0.08	0.09	0.54	3.58
	4	-0.41	1.08	-0.18	1.01	-0.42	0.66	2.74
	5	-0.08	2.74	-0.39	2.58	-1.02	1.56	2.04
Dye **3**	1	0.49	0.51	-0.1	0.49	-0.17	0.38	-1.19
	2	0.09	0.93	0.18	0.95	-0.03	0.43	0.58
	3	-0.41	0.99	-0.22	0.91	-0.45	0.63	2.69
	4	-0.12	2.42	0.08	2.36	-0.53	1.27	2.73
	5	-0.59	0.78	-1.17	0.45	-1.33	1.29	2.3
Dye **4**	1	0.29	0.29	-0.84	0.84	0.29	0.47	-0.14
	2	0.06	0.05	-0.6	0.61	-0.04	0.29	0.44
	3	0.15	-0.02	-0.77	0.74	-0.19	0.42	0.23
	4	0.06	-0.03	-0.52	0.49	-0.16	0.29	0.27
	5	-0.03	-0.04	-0.53	0.5	-0.18	0.31	0.63
Dye **5**	1	0.56	0.48	-2.75	2.1	1.83	1.54	-0.01
	2	1.62	-0.39	-1.43	1.46	0.27	1.04	-0.92
	3	0.93	0.07	-1.01	0.92	0.44	0.7	-0.79
	4	0.23	0.64	-1.08	0.85	0.92	0.76	-0.16
	5	-0.02	0.68	-0.71	0.55	0.82	0.64	0.03

The values throughout the table show remarkable qualitative consistency with the values given by FAS/TUDO, as given in Table 4.26. Generally the changes in lightness after reduction clearing with hydroxyacetone are small except for dye **1** at higher depths of shade only. The Δb* values of samples dyed with dyes **1** and **5** are quite significant, however, Δb* is positive in the case of dye **1** and negative in the case of dye **5**. A positive Δb* value (an increase in b*) indicates a shift of the colour towards yellow while a negative Δb* value (a decrease in b*) indicates a shift towards blue. The value Δa* is significant in the case of samples dyed with dye **2** only. Although, Δa* is positive for dye **3**, there is no particular trend across the depths of shades. The value Δb* is negative for dye **5** and is greater than Δa*. It is interesting to note that the value Δa* is significant for red dyes, dyes **2** and **3,** while Δb* is important for blue and yellow dyes, which are dyes **1**, **4** and **5**. Chroma of all the dyed samples increases after reduction clearing with hydroxyacetone. Change in chroma is similar to Δa* for red dyes and to Δb* for yellow and blue dyes. However, despite a negative Δb* value, the chroma of samples dyed with dyes **4** and **5** is positive.

Generally, the integ value increases after reduction clearing with hydroxyacetone. The only exception is dye **5**, in which case the integ value decreases, however this change is quite small and follows the same trend as is observed after reduction clearing with FAS/TUDO. The highest increase in integ value after reduction clearing with hydroxyacetone is observed for samples dyed with dyes **2** and **3**.

It is especially notable that where there are inconsistencies in trends in terms of the relationship between the colour change and depth of shade, there is, with only a few exceptions, qualitative consistency in the corresponding values given by the two reducing agents. There are also distinct similarities, although rather less consistently, with the colouristic trends following reduction with sodium dithionite (Table 4.14). Thus, the effect on colouristics of dyed polyester of reduction clearing is broadly and relatively independent of the reducing agent used, with the two organic reducing agents performing in a virtually identical way.

The colour differences of samples dyed with dye **3** as a result of reduction clearing with the organic reducing agents at the lower concentration are presented in Table 4.28. Comparison of the corresponding values when reduction clearing is carried out using higher concentration (Tables 4.26 & 4.27) of the two reducing agents show broad similarities in the

trends. The changes in integ values demonstrate that there is lower enhancement in colour strength as a result of clearing at the lower concentration, except for the single case of hydroxyacetone at a 5% depth of shade where it is marginally higher. In contrast, the increase in chroma is higher at the majority of depths of shades when clearing is carried with both agents at the lower concentration. A possible explanation for this behaviour may be that there is certain proportion of the surface dye whose removal results in a brightening of the colour and any dye removed in excess of that minimum threshold does not further improve the brightness of the dyed samples.

Table 4.28 Differences in colour parameters after reduction clearing with lower concentrations of FAS/TUDO and hydroxyacetone (HA)

		Shade (%)	ΔL*	Δa*	Δb*	ΔC*	ΔH*	ΔE (CMC)	Change in integ value
Dye **3**	Reduction cleared with FAS/ TUDO	1	1.24	1.34	-0.67	1.22	-0.87	1.07	-3.14
		2	0.3	1.24	0.0	1.21	-0.28	0.61	-0.18
		3	-0.08	0.65	-0.29	0.55	-0.44	0.43	0.59
		4	-0.19	0.48	-0.4	0.36	-0.51	0.48	0.91
		5	-0.28	1.56	-0.37	1.4	-0.78	1.04	2.19
	Reduction cleared with HA	1	1.49	1.51	-0.26	1.45	-0.49	1.14	-3.48
		2	0.38	1.33	0.02	1.3	-0.28	0.67	-0.5
		3	0.09	1.09	-0.25	1.0	-0.51	0.62	0.16
		4	-0.14	0.83	-0.55	0.66	-0.75	0.7	0.66
		5	-0.43	1.66	-0.77	1.4	-1.18	1.33	2.58

It is interesting to note that the washfastness properties are improved to a lesser degree at lower concentrations of the reducing agents while the chroma increases to a greater extent at lower concentrations of reducing agents. It is conceivable that, in some cases, the severity of reduction clearing required to provide excellent washfastness may not necessarily provide the conditions at which the enhancement in colouristics is optimal.

4.5.6 Scanning Electron Microscopy after Reduction Clearing with FAS/TUDO and Hydroxyacetone

Scanning electron micrographs of all the dyed samples before and after reduction clearing with FAS/TUDO and hydroxyacetone are shown in Figure 4.24 – Figure 4.38. All the dyed samples have relatively a higher amount of particles on the surface before reduction clearing (Figures 4.24, 4.27, 4.30, 4.33 and 4.36). Reduction clearing of the dyed samples using both FAS/TUDO and hydroxyacetone results in a comparatively cleaner fibre surface.

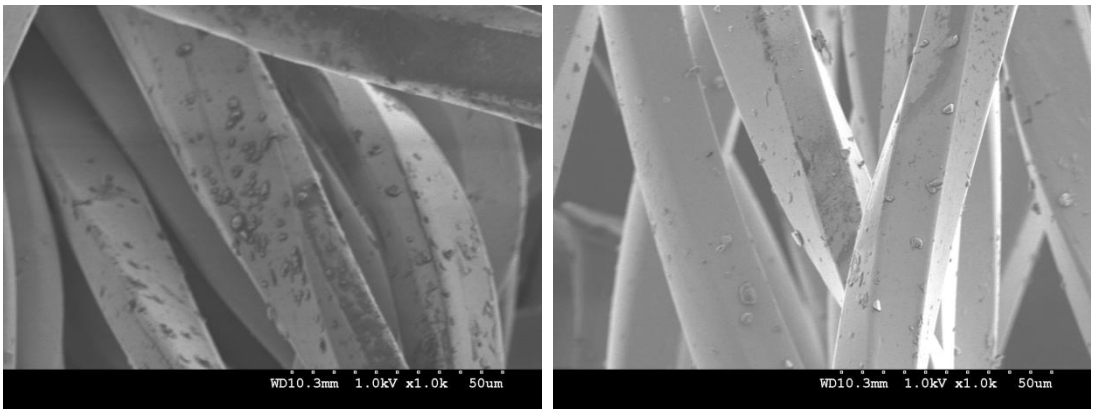


Figure 4.24 SEM images of samples dyed with dye **1** before reduction clearing

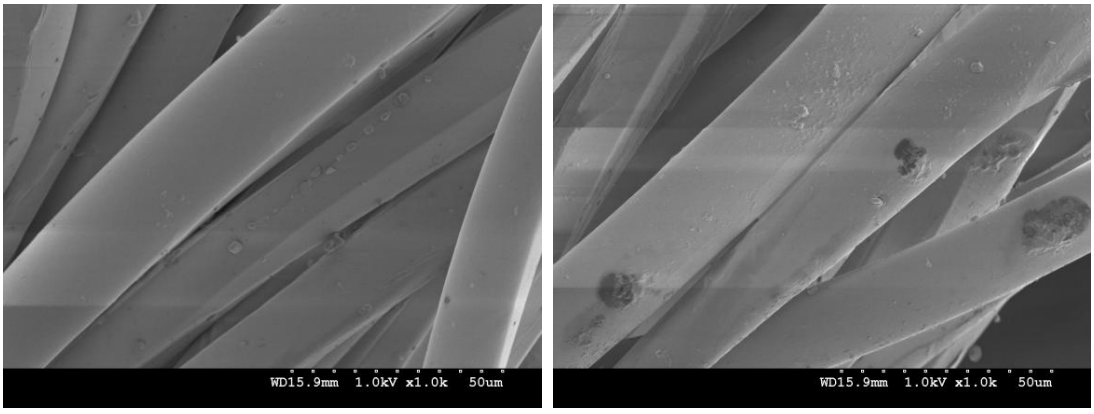


Figure 4.25 SEM images of samples dyed with dye 1 after reduction clearing with FAS/TUDO

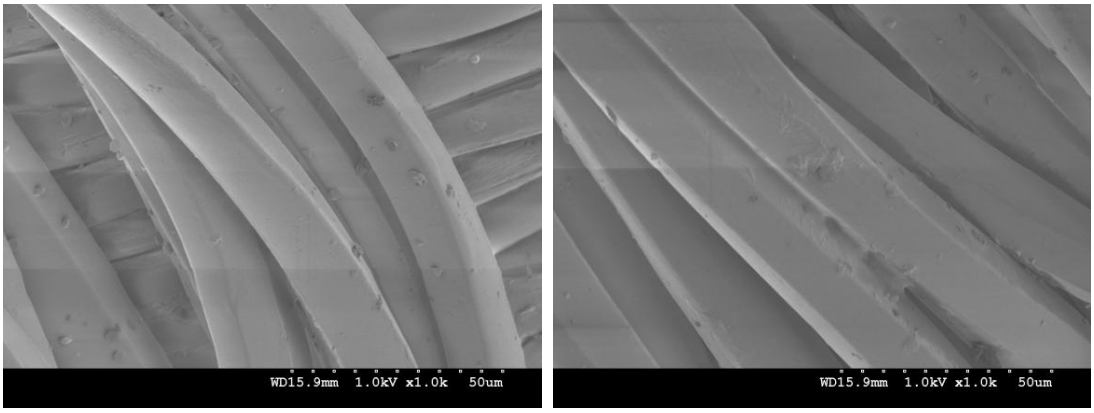


Figure 4.26 SEM images of samples dyed with dye **1** after reduction clearing with hydroxyacetone

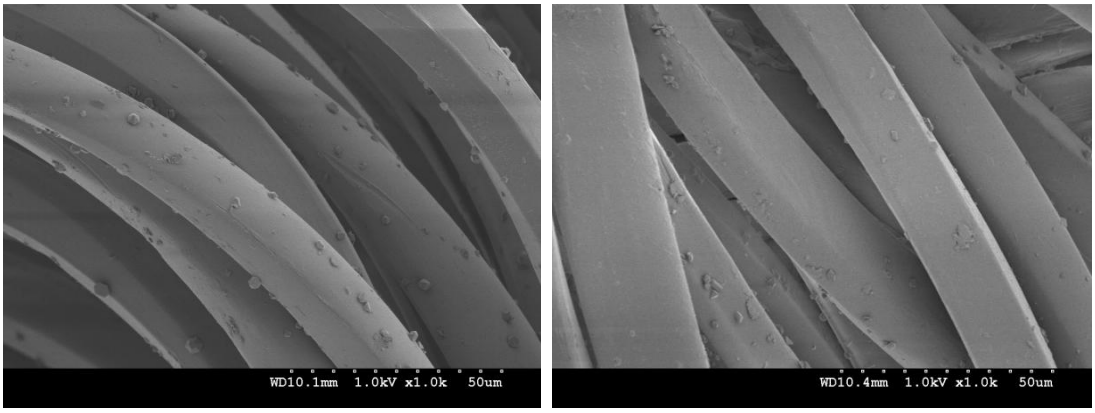


Figure 4.27 SEM images of samples dyed with dye **2** before reduction clearing

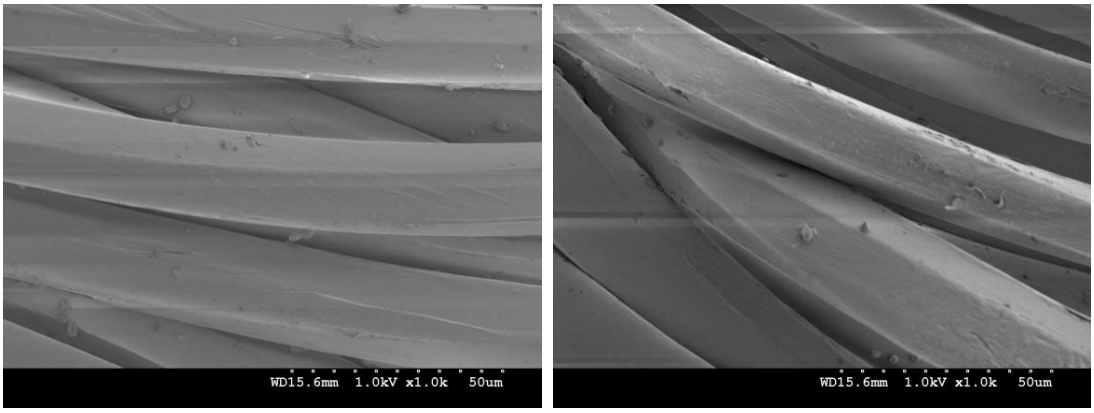


Figure 4.28 SEM images of samples dyed with dye **2** after reduction clearing with FAS/TUDO

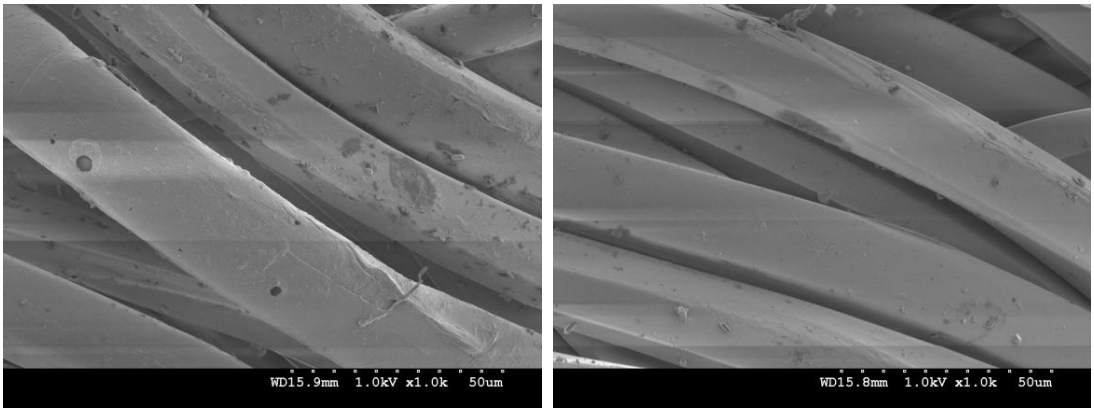


Figure 4.29 SEM images of samples dyed with dye **2** after reduction clearing with hydroxyacetone

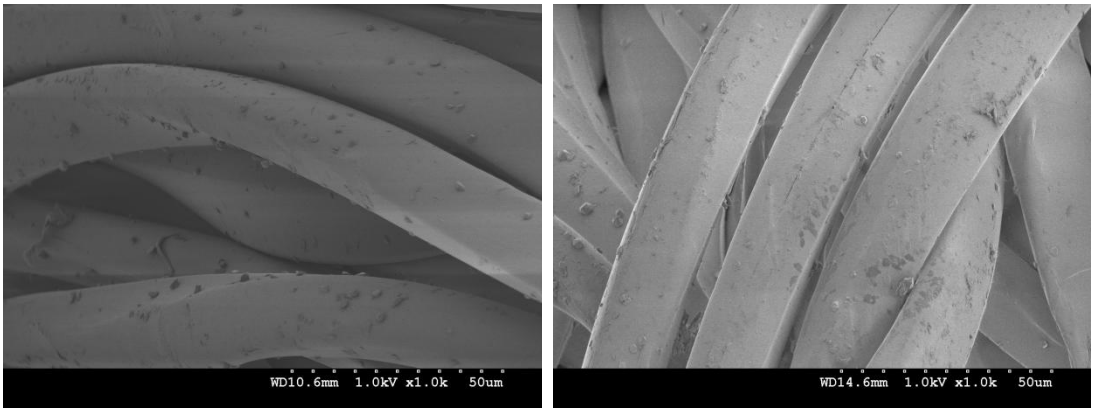


Figure 4.30 SEM images of samples dyed with dye **3** before reduction clearing

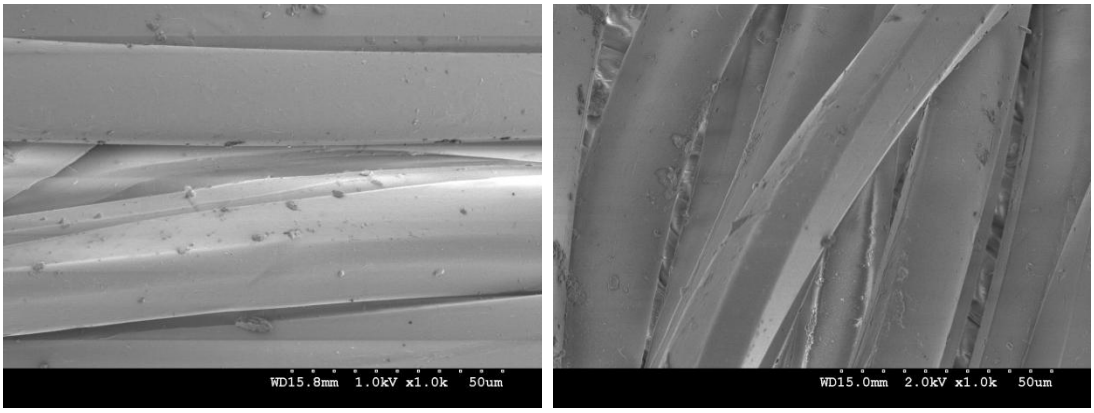


Figure 4.31 SEM images of samples dyed with dye **3** after reduction clearing with FAS/TUDO

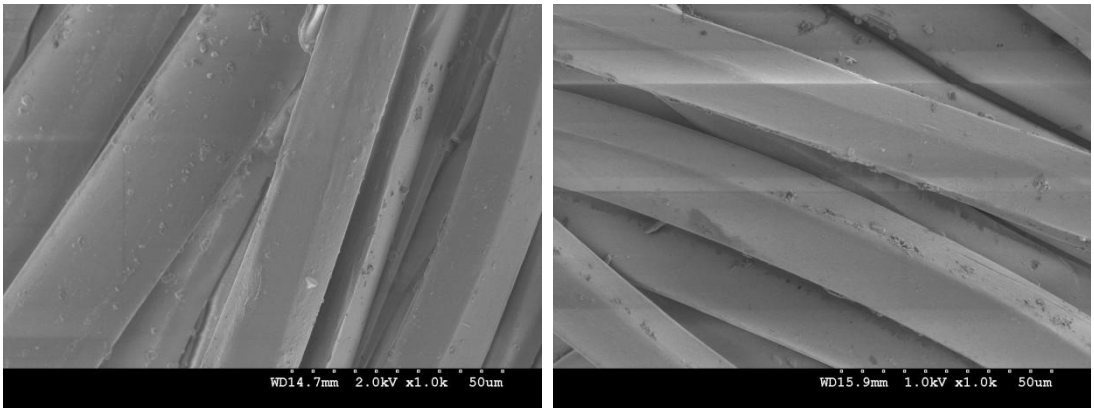


Figure 4.32 SEM images of samples dyed with dye **3** after reduction clearing with hydroxyacetone

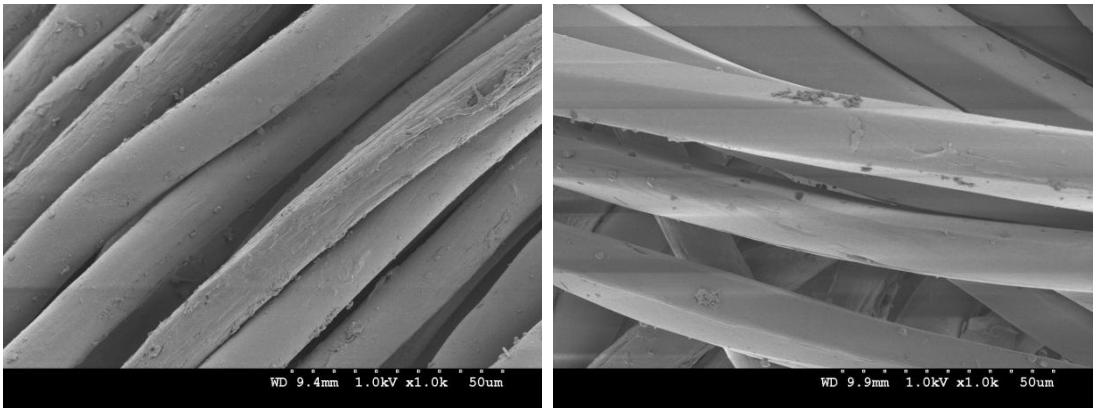


Figure 4.33 SEM images of samples dyed with dye **4** before reduction clearing

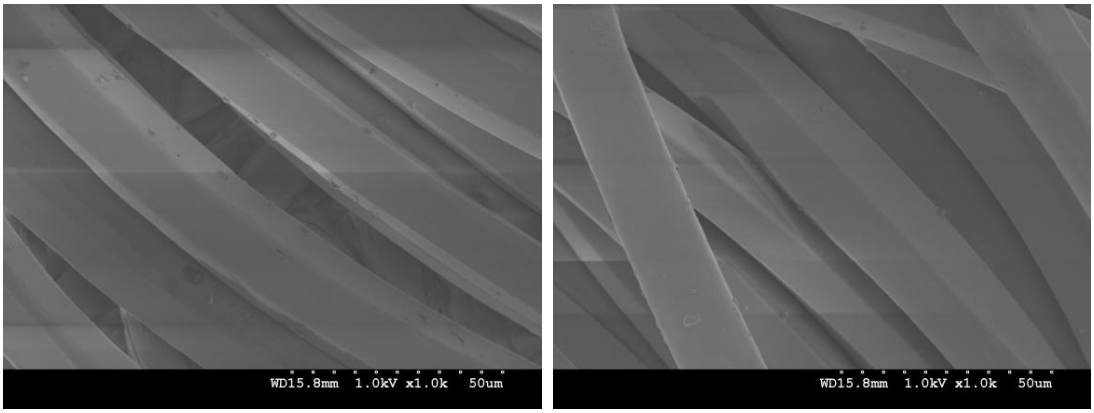


Figure 4.34 SEM images of samples dyed with dye **4** after reduction clearing with FAS/TUDO

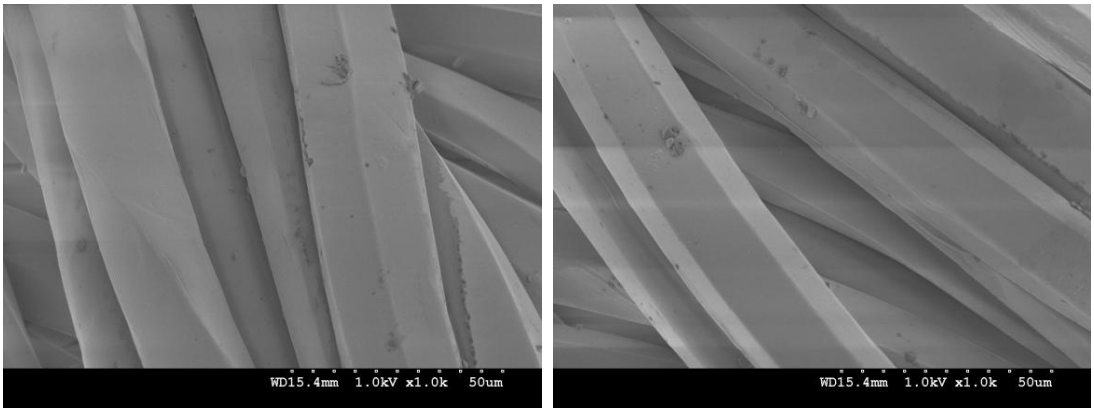


Figure 4.35 SEM images of samples dyed with dye **4** after reduction clearing with hydroxyacetone

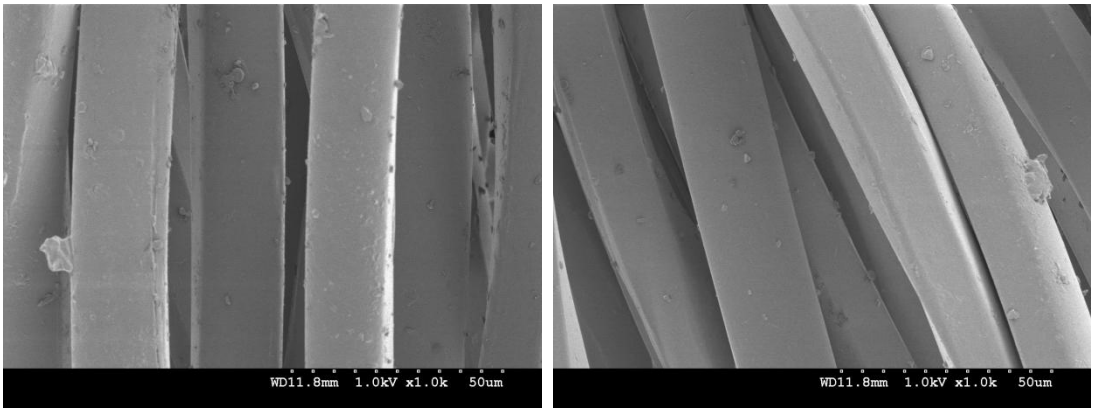


Figure 4.36 SEM images of samples dyed with dye **5** before reduction clearing

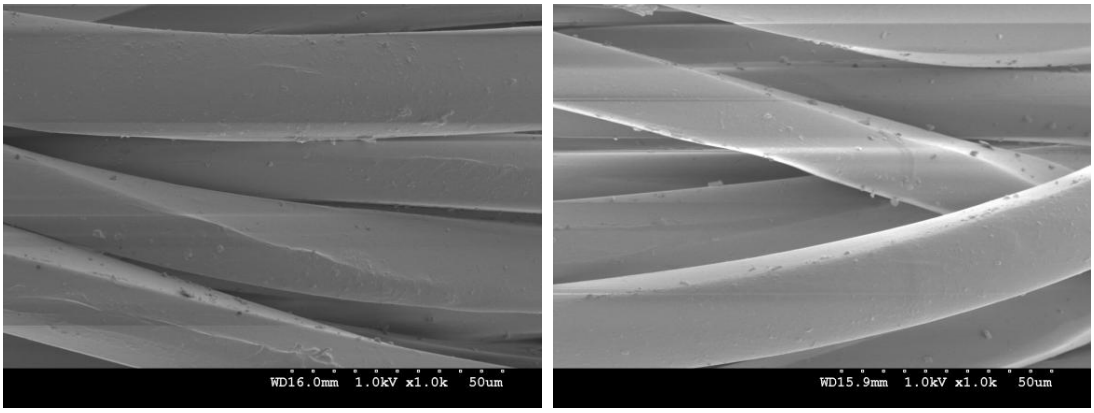


Figure 4.37 SEM images of samples dyed with dye **5** after reduction clearing with FAS/TUDO

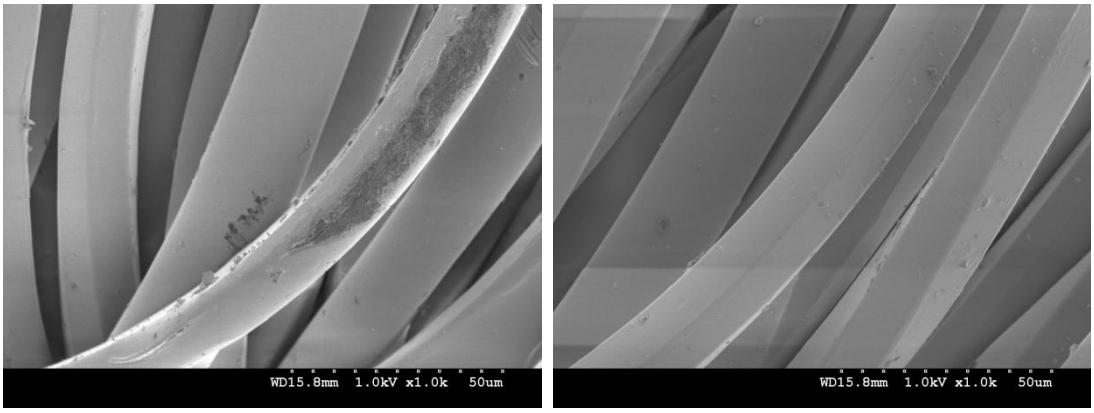


Figure 4.38 SEM images of samples dyed with dye **5** after reduction clearing with hydroxyacetone

SEM images of samples dyed with dye **3** using lower concentration of FAS/TUDO and hydroxyacetone are given in Figure 4.39 and Figure 4.40 respectively.

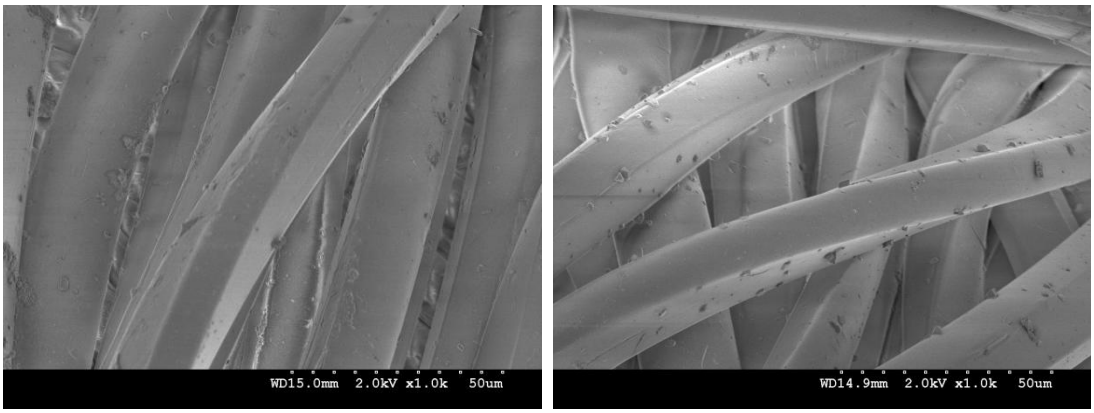


Figure 4.39 SEM images of sampled dyed with dye **3** after reduction clearing with lower concentration of FAS/TUDO

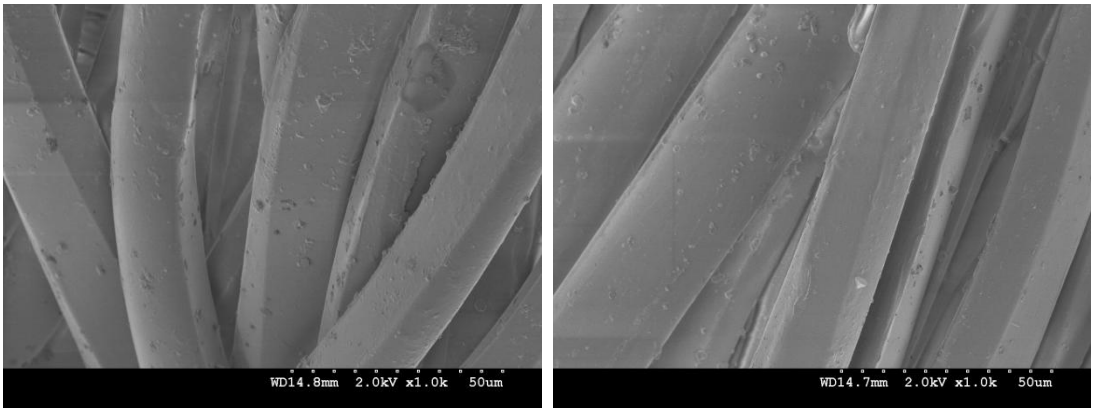


Figure 4.40 SEM images of samples dyed with dye **3** after reduction clearing with lower concentration of hydroxyacetone

A comparison with the corresponding samples reduction cleared using higher concentration of FAS/TUDO and hydroxyacetone (Figure 4.31 & Figure 4.32) shows that there is a greater number of particles present on the surface of samples reduction cleared using lower concentration of the reducing agents.

4.5.7 Reduction Clearing with Glucose

Glucose has been used as a reducing agent for sulphur dyes and as a stabilizer to prevent over-reduction during vat dyeing [89, 126]. Recently, its use has been reported for the reduction of vat dyes [107]. In this study, glucose has been employed for the reduction clearing of polyester which has been dyed with selected disperse dyes. It is reported that glucose is a mild reducing agent and is only effective for the reduction of dyes at high temperatures, around 90°C. However, the reduction process starts at about 60 – 70°C. There are reports in which glucose is said to reduce indigo at about 65°C [107]. It follows from the discussion in Section 2.6.3 that temperature and alkalinity are the two major factors which influence the reducing properties of glucose. Thus, in this study concerning the optimization of conditions of reduction clearing with glucose, the first parameter selected for optimisation was temperature, followed by alkalinity. The optimisation experiments were carried out for samples dyed with dye **3** at 3% o.m.f. only. The optimised conditions were then used for the reduction clearing of the samples dyed with the other four dyes at 3% o.m.f. A discussion of the optimization experiments with glucose is given in the following section.

4.5.8 Optimisation Experiments using Glucose

The initial experiments were carried out at a high concentration of glucose as the reported redox potential of glucose is quite low compared with sodium dithionite [14, 89]. All of the other parameters were set at the values used for reduction clearing with sodium dithionite, which are a temperature of 70°C for 20 min. Table 4.29 lists the change in absorbance values of the acetone extracts of samples dyed with dye **3** (3% o.m.f.) when reduction cleared with glucose for optimisation of the conditions.

Table 4.29 Absorbance values of the acetone extract and washfastness properties of the samples dyed with dye **3** after reduction clearing with glucose for optimisation

Conc. of glucose (g l^{-1})	0	0	60			30		10			5			2	
Conc. of alkali (g l^{-1})	0	0	2		8	2	8	20	8	8	8	4	4	4	2
Temperature (°C)	70	90	70	90	70	90	90	90	90	90	90	90	90	90	90
SynperonicBD-100 (ml l^{-1})	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1
Time (min)	20	20	20	20	20	20	20	20	40	20	20	20	40	20	20
Absorbance	1.10	0.92	0.44	0.30	0.29	0.36	0.09	0.47	0.12	0.16	0.35	0.28	0.40	0.22	0.09
Washfastness - staining															
Wool	4	4	4-5	5	5	4-5	5	4-5	5	5	4-5	5	5	5	5
Acrylic	4-5	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5
Polyester	3-4	3-4	4-5	4-5	4-5	4-5	5	4-5	5	5	4-5	4-5	4-5	4-5	4-5
Nylon	2	2	3-4	4	4	3-4	4-5	2-3	4	3-4	3-4	4	3	3-4	4
Cotton	4-5	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5
Acetate	2-3	2-3	4	4	4-5	3-4	4-5	3-4	4-5	4	3-4	4	3-4	3-4	4

Initially, sodium hydroxide was used at a concentration of 2 g l^{-1}. The concentration of glucose was then decreased to study the effect on the level of surface dye and washfastness properties. However, it was observed that a gradual decrease in the concentration of glucose did not result in a corresponding decrease in the absorbance values of the cold acetone extract of the treated samples (Table 4.29).

Similarly, it became clear from the data in Table 4.29 that a higher concentration of sodium hydroxide did not improve the removal of surface dye as indicated by the absorbance values of the acetone extract. On the other hand, an increase in temperature led to a decrease in the absorbance values of the acetone extract of the glucose-cleared sample, thus indicating more efficient removal of surface dye. The time period of reduction clearing was also increased to 40 minutes to establish whether longer times provided some advantage during the removal treatment. However, results of the absorbance of the acetone extract of the treated samples obtained for a 40 minutes treatment do not show any significant improvement over the absorbance obtained for a 20 minutes treatment.

The washfastness properties of these samples were also determined and the final assessment concerning the optimised conditions was made by considering both the concentration of the dye in the acetone extract and washfastness results. Two control experiments without glucose and alkali were also carried out at 90°C and 70°C for 20 minutes to observe the effect of hot water only. It is evident from the data in Table 4.29 that although the control treatments at the specified temperature decrease the absorbance of the acetone extract of the treated samples, the washfastness properties remain poor (stain rating of 2 on nylon).

The washfastness properties after reduction clearing with glucose at 70°C are only moderate. This feature was found to improve either by increasing the concentration of alkali or the temperature of the treatment. However, an increase in the concentration of alkali above 8 g l^{-1} adversely affected the washfastness properties as observed at a concentration of 10 g l^{-1} glucose with double the amount of sodium hydroxide (20 g l^{-1}). It appears therefore that there is a certain ratio of glucose to sodium hydroxide at which washfastness properties are optimum. Thus, on the basis of absorbance of the acetone extract and washfastness results of the treated samples, a concentration of 2 g l^{-1} glucose and 2 g l^{-1} sodium hydroxide at 90°C appears to be the optimum conditions for the reduction clearing with glucose in this case.

4.5.9 Assessment of Surface Dye Removal after Reduction Clearing with Glucose

After the optimisation of conditions for reduction clearing of samples dyed with dye **3** with glucose, the samples dyed with other four dyes (3% o.m.f.) were then reduction cleared with glucose under the optimised conditions.

Table 4.30 Comparison of absorbance values of all the dyed samples (3% o.m.f.) after reduction clearing with sodium dithionite, FAS/TUDO, hydroxyacetone and glucose

	Untreated		Sodium dithionite		FAS/TUDO		Hydroxyacetone		Glucose	
	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.
Dye **1**	440	1.24	437	0.12	439	0.14	438	0.15	435	0.03
Dye **2**	510	1.86	509	0.15	509	0.11	509	0.08	498	0.04
Dye **3**	512	1.92	508	0.88	511	0.12	494	0.16	474	0.09
Dye **4**	630	0.62	629	0.20	630	0.10	630	0.28	631	0.14
Dye **5**	666	0.36	666	0.06	665	0.05	664	0.04	623	0.06

A comparison of the absorbance values of the acetone extract of the samples dyed with all of the five dyes at the 3% depth of shade after reduction clearing with all the four reducing agents is given in Table 4.30. It is observed that the absorption maximum for dyes **1** and **4** remains almost the same after reduction clearing with glucose, whereas the absorption maxima of dyes **2**, **3** and **5** is changed significantly after reduction clearing with glucose. The absorption maximum shifts towards lower wavelength after reduction clearing with all of the reducing agents. This shift is more pronounced after reduction clearing with glucose for dyes **2**, **3** and **5**, the magnitude of shift increasing in that order. A shift towards shorter wavelength may indicate the presence of yellow coloured compounds in the extract which are possibly formed as a result of dye degradation. The greater shift towards yellow in the case of glucose clearing may be explained on the basis of the reduction mechanism using glucose as discussed in Section 2.6.3. Glucose undergoes complex degradation in alkaline medium resulting in the formation of various intermediates having enediol structures, which are reported to be slightly coloured [102]. There is thus a possibility that the absorbance values are not a completely accurate indicator of surface dye removal after reduction clearing with glucose in those cases.

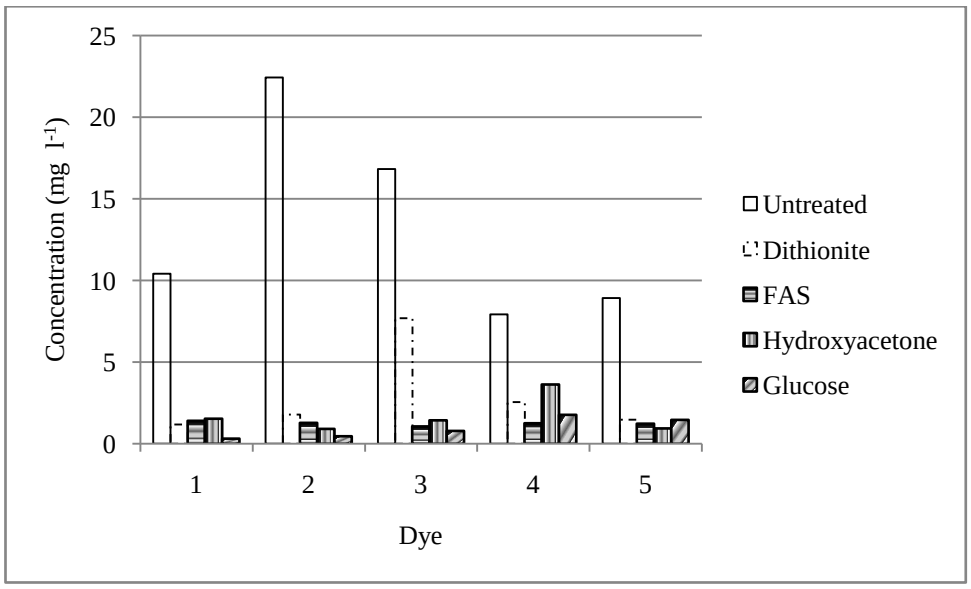


Figure 4.41 Concentration of dyes in acetone extract after reduction clearing with various reducing agents

It is observed from the data in Table 4.31 and Figure 4.41 that for dye **5**, both sodium dithionite and glucose result in a similar concentration of dye in the acetone extract after reduction clearing. Another notable trend is that glucose is more effective under the conditions used for removal of azo dyes when compared with the anthraquinone dyes. In fact, glucose is more effective than FAS/TUDO and hydroxyacetone for the reduction clearing of the three azo dyes, **1**, **2** and **3**. FAS/TUDO is slightly better than glucose in the removal of surface dye for the samples dyed with the two anthraquinone dyes, **4** and **5**. Reduction clearing with FAS/TUDO results in comparable concentrations of the dyes in the acetone extract of all the dyed samples while hydroxyacetone is least effective for dye **4** as indicated by a high concentration of 3.63 mg l^{-1}.

Table 4.31 Concentration (mg l^{-1}) of dyes in acetone extract after reduction clearing with various agents

	Untreated	Reduction cleared with			
		Sodium dithionite	FAS/TUDO	Hydroxyacetone	Glucose
Dye **1**	10.4	1.17	1.41	1.53	0.39
Dye **2**	22.4	1.79	1.28	0.92	0.46
Dye **3**	16.8	7.69	1.07	1.44	0.79
Dye **4**	7.9	2.54	1.3	3.63	1.78
Dye **5**	8.9	1.47	1.2	0.94	1.47

Figure 4.42 shows a graph which illustrates a comparison of the percentage of surface dye removal of the samples dyed with five dyes after reduction clearing with sodium dithionite, FAS/TUDO, hydroxyacetone and glucose. It is observed that glucose performs better than sodium dithionite in the removal of surface dye from the samples dyed with all of the dyes. Even in the case of samples dyed with dye **3**, which showed poor response to reduction clearing with sodium dithionite, with only about 50% of the surface dye being removed, glucose performs significantly better, by removing about 90% of the surface dye. The responses of dyes **1**, **2**, **4** and **5** to reduction clearing with sodium dithionite and glucose are comparable, within a range of around 10% of each other, with glucose performing slightly better. However, in the case of samples dyed with dye **3**, the difference between the efficiency of the two reducing agents, sodium dithionite and glucose, becomes significant, with glucose performing about 40% better.

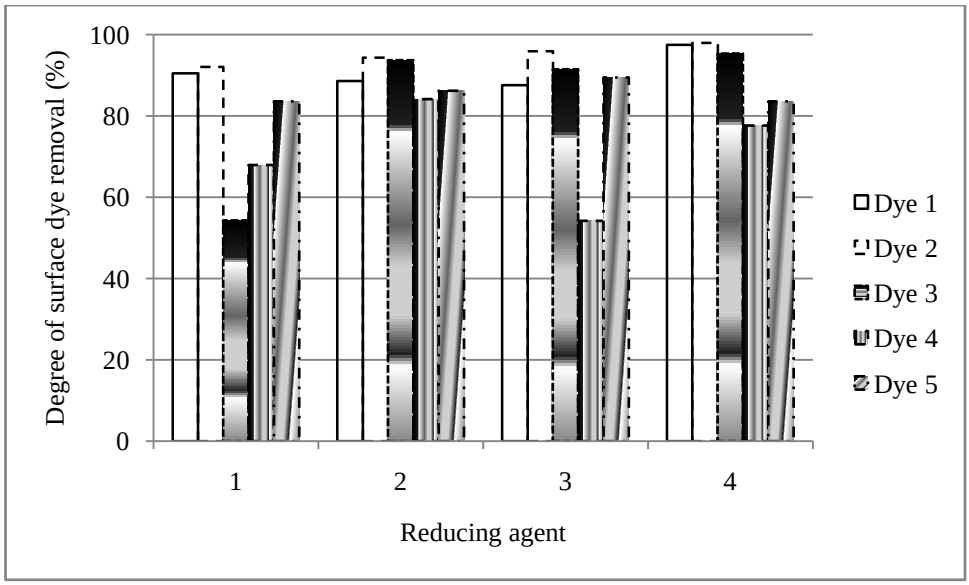


Figure 4.42 Degree of surface dye removal after reduction clearing with various reducing agents, 1 - sodium dithionite, 2 - FAS/TUDO, 3 - hydroxyacetone, 4 - glucose

4.5.10 Washfastness Properties after Reduction Clearing with Glucose

The washfastness properties of the samples reduction-cleared with glucose are given in Table 4.32. As the results of washfastness of samples reduction cleared with sodium dithionite showed no significant change in colour, only the results of the staining of the adjacent multifibre fabric are given for reduction clearing with glucose. It is observed that reduction clearing with glucose improves the washfastness properties of all of the dyes to very good – excellent, except for dye **4**. Even dye **3** responds well to reduction clearing by glucose and nylon staining is decreased giving a rating of 4.

Table 4.32 Washfastness of all the dyed samples after reduction clearing with sodium dithionite and glucose

		Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
Dye **1**	Untreated	5	5	5	4	5	4
	Dithionite	5	5	5	5	5	5
	Glucose	5	5	5	5	5	5
Dye **2**	Untreated	4	4-5	3	2-3	4-5	1-2
	Dithionite	5	5	5	5	5	4-5
	Glucose	5	5	5	4-5	5	4-5
Dye **3**	Untreated	4	5	3-4	2-3	5	2-3
	Dithionite	4-5	5	4	3-4	5	3-4
	Glucose	5	5	4-5	4	5	4
Dye **4**	Untreated	4	5	4	2-3	4-5	3-4
	Dithionite	4-5	5	4-5	3-4	5	4-5
	Glucose	4-5	5	4	3-4	5	4-5
Dye **5**	Untreated	4-5	5	5	5	5	5
	Dithionite	5	5	5	5	5	5
	Glucose	5	5	5	4	5	5

A comparison of the washfastness of the dyed samples after reduction clearing with sodium dithionite and glucose as given in Table 4.32 shows that glucose improves the washfastness properties to a marginally better level than that of sodium dithionite. An interesting observation is made in the case of dye **5**, in that staining on nylon is increased after reduction clearing with glucose. The untreated fabric samples dyed with dye **5** give a rating of 5 on nylon as there is no staining. This rating is maintained after reduction clearing with sodium dithionite. However after reduction clearing with glucose, the stain rating decreases to 4 indicating that there is a slight staining on nylon. A possible explanation for this anomaly may be proposed based on the reduction mechanism of glucose. It is known that glucose undergoes complex oxidative degradation in alkaline media and produces slightly coloured intermediates. This slight staining on nylon may be due to these coloured intermediate compounds or some products which are formed as a result of dye reduction. The colour of this stain on nylon is blue and thus it is more plausible that the staining is caused by dye degradation. Reduction clearing of samples dyed with dye **5** with hydroxyacetone also resulted in

staining of nylon in the multifibre fabric (Table 4.22). Although, in the case of samples dyed with dye **4**, the improvement in the washfastness properties after reduction clearing with glucose is similar to that after reduction clearing with sodium dithionite and hydroxyacetone, it is less than FAS/TUDO. Similar to glucose, hydroxyacetone also undergoes a complex sequence of steps under alkaline conditions resulting in the formation of various intermediate compounds. Although most of these intermediates have unconfirmed identities, they all are reported to have enediol structures. Consequently, it may be inferred that reduction clearing with glucose and hydroxyacetone might have similar effect on the dyed samples.

The results of the washfastness tests also support the proposition made in Section 4.5.9 based on the results of the percentage dye removal that glucose is comparatively more efficient for the reduction clearing of samples dyed with azo dyes **1**, **2** and **3** than anthraquinone dyes, **4** and **5**.

4.5.11 Rubfastness Properties after Reduction Clearing with Glucose

The rubfastness of the dyed samples after reduction clearing with sodium dithionite and glucose is given in Table 4.33.

Table 4.33 Rubfastness of the dyed samples after reduction clearing with sodium dithionite and glucose

	Untreated		Sodium dithionite		Glucose	
	Dry	Wet	Dry	Wet	Dry	Wet
Dye **1**	4-5	4-5	5	5	5	5
Dye **2**	4	4	5	5	5	5
Dye **3**	4	4-5	4-5	5	5	4-5
Dye **4**	4-5	4	5	5	5	4-5
Dye **5**	5	5	5	5	5	5

The results given in Table 4.33 demonstrate that glucose improves the rubfastness properties of the dyed samples to a level as good as sodium dithionite. However, in the case of dyes **3** and **4**, wet rubfastness after reduction clearing with glucose is marginally lower than after sodium dithionite is used. This staining may be due to dye degradation products or glucose derivatives formed during the reduction process as discussed in Section 4.5.10.

4.5.12 Colour Properties after Reduction Clearing with Glucose

The colour properties of the all the dyed samples (3% o.m.f.) after reduction clearing with glucose are given in Table 4.34. There are only small changes in lightness while significant changes are observed in the chroma of all of the dyed samples except for dye **5**. A similar trend is observed in the integ value which undergoes exceptional changes on reduction clearing with glucose except for dye **5** whose integ value only changes slightly. An increase in both lightness and chroma usually appears as an increase in brightness of the colour. Only samples dyed with dyes **1** and **5** thus get brighter according to this definition.

Table 4.34 Colour properties of the dyed samples (3% o.m.f.) after reduction clearing with glucose

		L*	a*	b*	C*	h°	Integ value
Dye **1**	Untreated	77.1	18.6	99.26	100.98	79.38	26.93
	Reduction cleared	78.03	18.11	102.77	104.35	80.01	30.56
Dye **2**	Untreated	24.30	33.71	6.98	34.43	11.7	48.49
	Reduction cleared	23.6	36.48	7.41	37.23	11.49	55.66
Dye **3**	Untreated	23.40	32.02	8.05	33.02	14.11	52.51
	Reduction cleared	22.63	33.64	8.27	34.64	13.81	58.75
Dye **4**	Untreated	22.30	6.14	-30.37	30.98	281.43	38.78
	Reduction cleared	21.79	6.5	-31.22	31.89	281.76	41.52
Dye **5**	Untreated	41.05	-13.43	-33.86	36.42	248.37	15.27
	Reduction cleared	41.86	-13.33	-35.58	37.99	249.47	15.15

When compared with sodium dithionite, FAS/TUDO and hydroxyacetone, glucose produces more or less consistently the largest differences in the colour of the dyed samples (Table 4.35). The only exception is dye **5** in which case the effect of glucose on colour properties is comparable to the other reducing agents. These results correlate with the concentration of the dyes in the cold acetone extract of the treated samples and washfastness properties. In the case of dye **1**, glucose removes the greatest amount of the surface dye when compared with the other reducing agents. Thus, it produces the largest change in integ value while the fastness properties are also improved to a comparable value. However, dye **1** already has good washfastness properties (nylon

staining is 4) and both reducing agents, sodium dithionite and glucose, improve the ratings to excellent (Table 4.32).

Table 4.35 Differences in colour parameters after reduction clearing with various reducing agents

		ΔL*	Δa*	Δb*	ΔC*	ΔH*	ΔE (CMC)	Change in integ value
Dye **1**	Sodium dithionite	1.16	0.41	2.35	2.38	-0.01	0.81	0.76
	FAS/TUDO	0.82	0.45	2.3	2.35	-0.05	0.75	1.54
	Hydroxyacetone	1.05	0.74	2.76	2.85	-0.25	0.92	1.67
	Glucose	0.93	-0.5	3.51	3.37	1.12	1.22	3.63
Dye **2**	Sodium dithionite	-0.19	0.89	-0.38	0.8	-0.51	0.56	1.32
	FAS/TUDO	-0.91	-0.07	0.14	-0.04	0.15	0.66	4.5
	Hydroxyacetone	-0.76	-0.1	0.07	-0.08	0.09	0.54	3.58
	Glucose	-0.71	2.77	0.43	2.8	-0.14	1.40	7.17
Dye **3**	Sodium dithionite	-0.14	0.78	-0.21	0.71	-0.4	0.46	2.75
	FAS/TUDO	0.02	1.03	-0.3	0.93	-0.54	0.6	0.35
	Hydroxyacetone	-0.41	0.99	-0.22	0.91	-0.45	0.63	2.69
	Glucose	-0.77	1.62	0.22	1.62	-0.18	0.97	6.24
Dye **4**	Sodium dithionite	0.26	0.15	-0.48	0.5	0.05	0.32	-0.65
	FAS/TUDO	0.13	-0.1	-0.74	0.7	-0.26	0.43	0.4
	Hydroxyacetone	0.15	-0.02	-0.77	0.74	-0.19	0.42	0.23
	Glucose	-0.51	0.36	-0.85	0.91	0.18	0.61	2.74
Dye **5**	Sodium dithionite	0.06	1.01	-1.18	0.75	1.37	0.98	-0.02
	FAS/TUDO	1.15	0.06	-1.24	1.14	0.5	0.85	-0.97
	Hydroxyacetone	0.93	0.07	-1.01	0.92	0.44	0.7	-0.79
	Glucose	0.81	0.1	-1.72	1.57	0.71	0.95	-0.12

The integ value of samples dyed with dye **2** is also increased by all of the four reducing agents. However, glucose produces the largest increase. Interestingly, the chroma of samples dyed with dye **2** is changed to a significant degree by glucose only while the changes produced by the other reducing agents are very small. In this case too, glucose gives the highest removal of surface dye although the percentage of surface dye removed by all the reducing agents is comparable. The washfastness properties of the

samples dyed with dye **2** are also improved by glucose to a comparable level to that of sodium dithionite. In the case of samples dyed with dye **3**, sodium dithionite was only able to remove about 50% of the surface dye whereas glucose removed about 90% of the surface dye. However, the washfastness properties are improved to only a slightly higher degree by glucose. In the case of dye **3** also, the integ value is increased to the greatest degree by glucose. The higher efficiency of glucose in the removal of dye **3** from the surface does not translate into a significantly enhanced improvement of the washfastness properties compared with that given by sodium dithionite. This means that even a small amount of residual dye present on the fibre surface can contribute to less than excellent washfastness properties. The affinity of the dye for the adjacent fibres besides the amount of surface dye present also plays an important role in determining the washfastness. In the case of dye **4**, glucose is slightly less efficient than FAS/TUDO but better than sodium dithionite and hydroxyacetone in the removal of surface dye. Hydroxyacetone performs less well than sodium dithionite in the removal of surface deposits of dye **4**. Nevertheless, the integ value is influenced significantly after reduction clearing with glucose. The washfastness properties of samples dyed with dye **4** are comparable after reduction clearing with glucose and sodium dithionite. The integ value of samples dyed with dye **5** changes only slightly (less than 1) after reduction clearing with all of the reducing agents and this change is negative in all four cases, i.e., the integ value decreases after reduction clearing with all the four reducing agents. This trend is not observed with any other dye except for dye **4** in one instance only. However, the chroma of samples dyed with dye **5** increases after reduction clearing with all the four reducing agents. Glucose is not superior to sodium dithionite in the removal of surface deposits of dye **5** with both reducing agents giving the same concentration of dye in the acetone extract. However, the washfastness rating is decreased slightly after reduction clearing with glucose which may be due to the products of dye reduction as proposed in Section 4.5.10.

4.5.13 Scanning Electron Microscopy after Reduction Clearing with Glucose

The scanning electron micrographs of the dyed samples after reduction clearing with glucose are shown in Figures 4.44, 4.46, 4.48, 4.50 and 4.52. These images show a significantly cleaner fibre surface as compared to the dyed samples before reduction clearing (Figures 4.43, 4.45, 4.47, 4.49 & 4.51). However, some particles which may be dye deposits can be seen on the surface of sampled dyed with dye **3** after reduction clearing with glucose as shown in Figure 4.48. These results are correlated with the results of the washfastness tests. The washfastness properties of samples dyed with dye **3** are improved to slightly better than after reduction clearing with sodium dithionite but are marginally less than the washfastness properties of the samples dyed with dye **2** (Table 4.32). A probable explanation for this difference between the two dyes has been suggested as the presence of the ester groups in dye **2** which render the dye potentially hydrolysable and thus hydrophilic as compared to dye **3**.

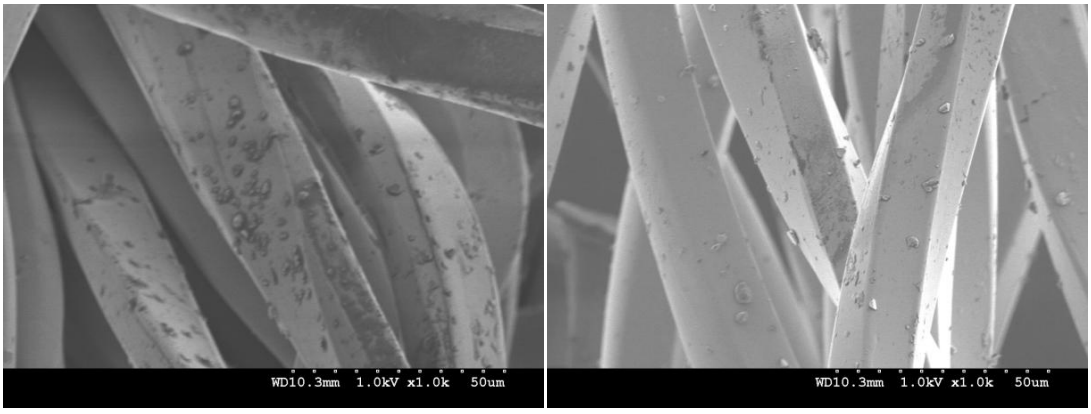


Figure 4.43 SEM images of samples dyed with dye **1** before reduction clearing

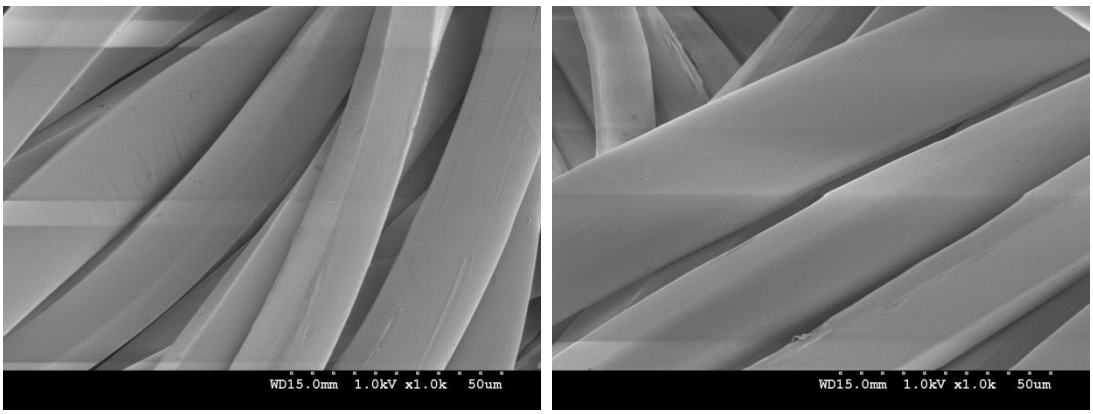


Figure 4.44 SEM images of samples dyed with dye **1** after reduction clearing with glucose

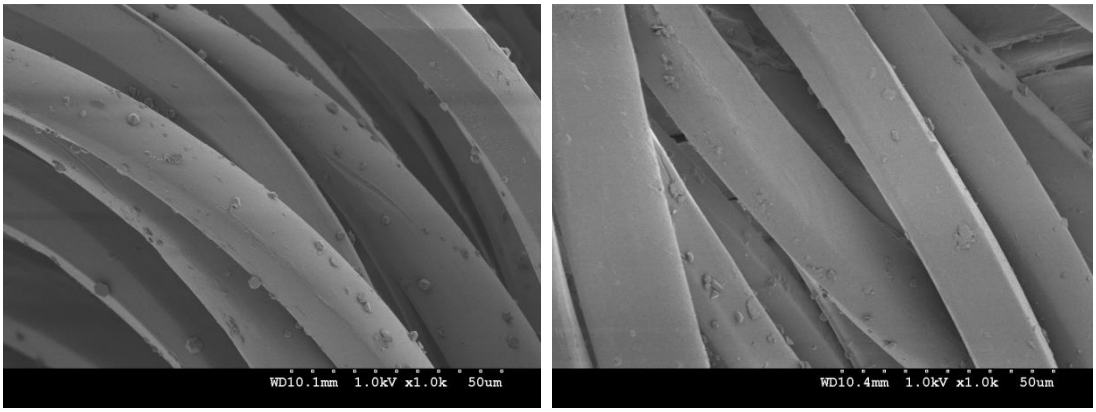


Figure 4.45 SEM images of samples dyed with dye **2** before reduction clearing

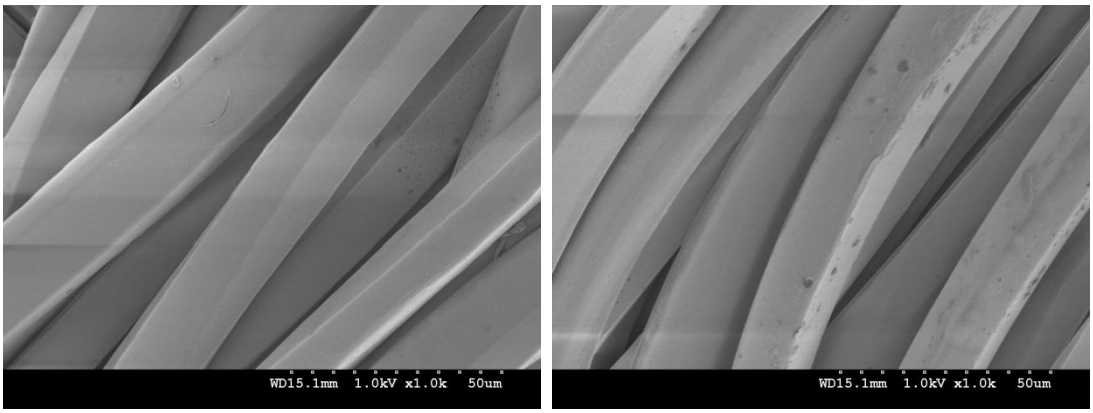


Figure 4.46 SEM images of samples dyed with dye **2** after reduction clearing with glucose

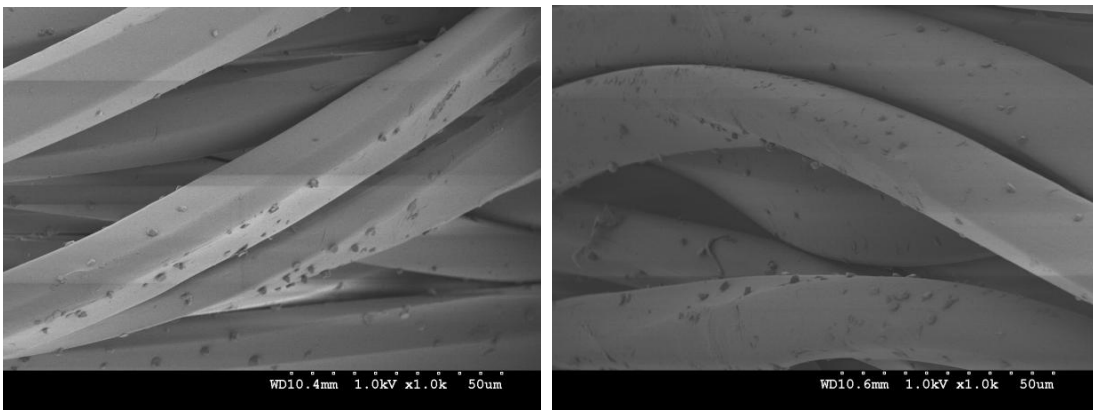


Figure 4.47 SEM images of samples dyed with dye **3** before reduction clearing

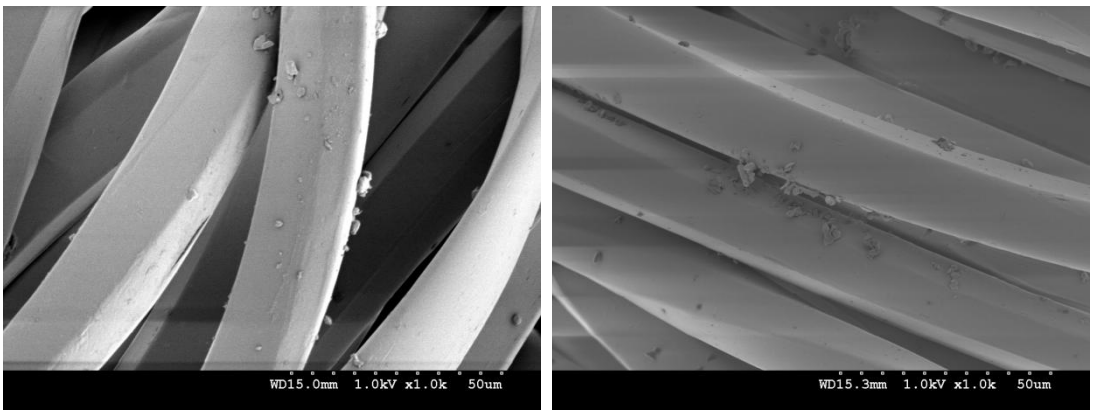


Figure 4.48 SEM images of samples dyed with dye **3** after reduction clearing with glucose

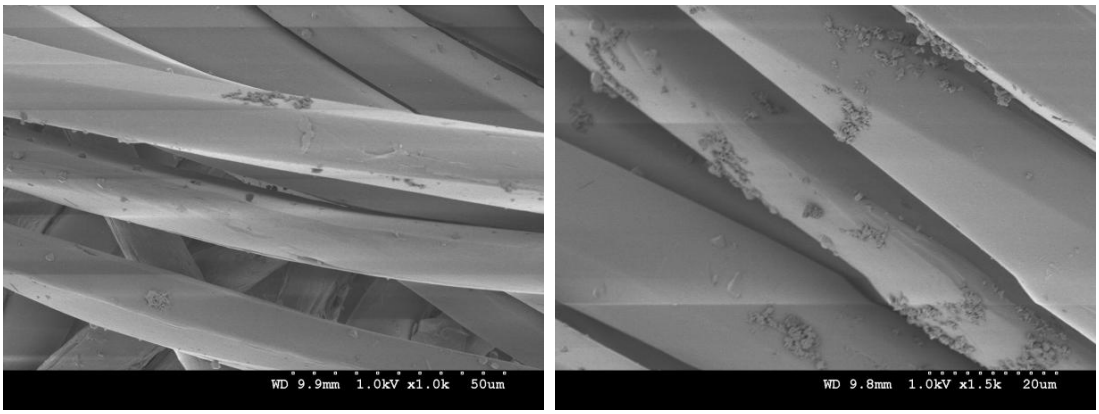


Figure 4.49 SEM images of samples dyed with dye **4** before reduction clearing

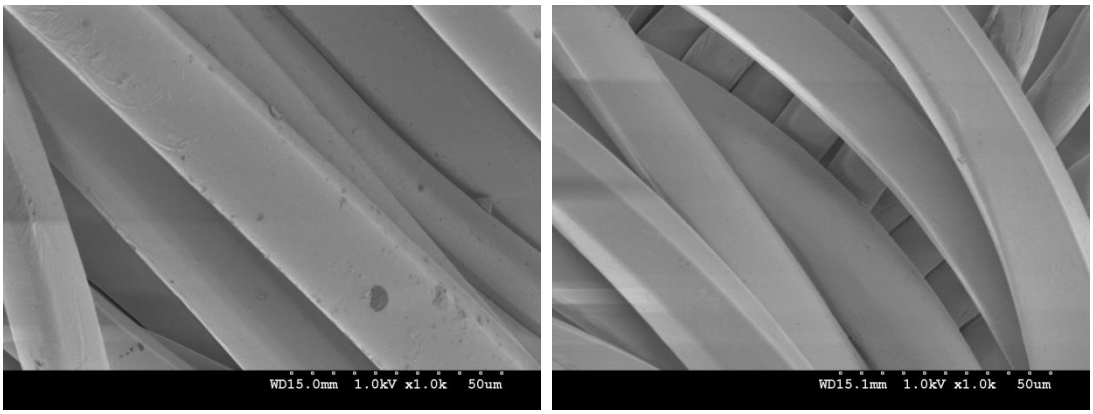


Figure 4.50 SEM images of samples dyed with dye **4** after reduction clearing with glucose

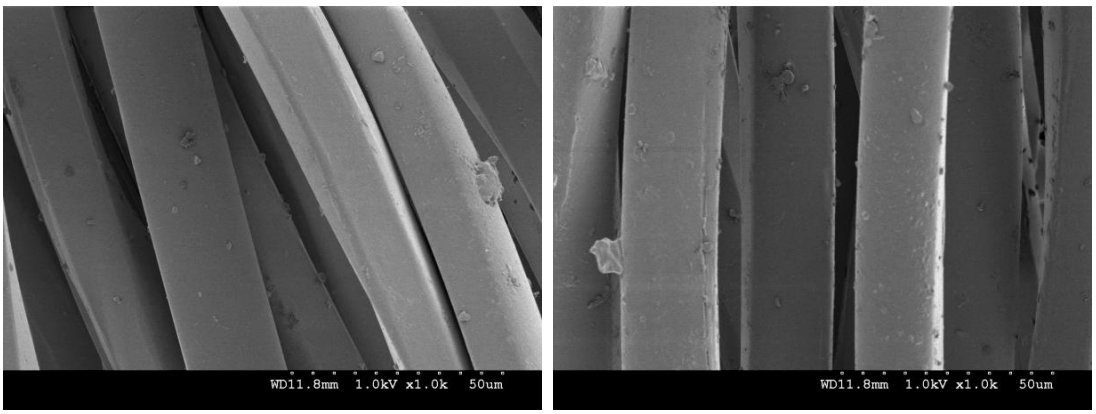


Figure 4.51 SEM images of samples dyed with dye **5** before reduction clearing

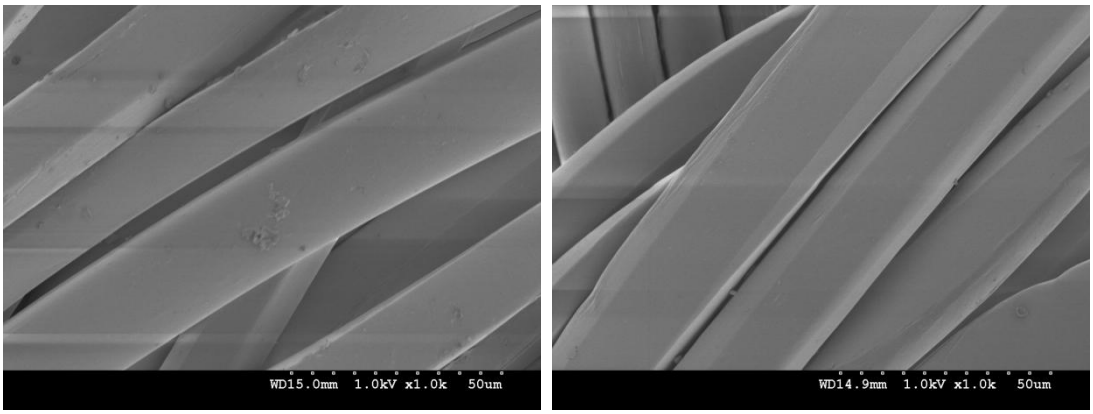


Figure 4.52 SEM images of samples dyed with dye **5** after reduction clearing with glucose

4.6 Detergent-based Wash-off Treatment

There has been a growing belief that the industrial importance of reduction clearing is diminishing. This has been suggested because of, among numerous factors, the improved dispersion properties of disperse dyes which has become possible due to advances in dye formulation and manufacturing processes and the availability of dyeing machines with efficient rinsing systems [6, 15]. There has been a recent report where it has been suggested that reduction clearing may be replaced by a detergent based wash-off treatment [18]. In this research, a comparison is made with the outcome of the detergent-based wash-off treatment which has previously been reported. Thus, this washing off treatment was also carried out for polyester fabric samples dyed with all of the five disperse dyes at the selected five depths of shade. The study described in this thesis includes polyester fabrics dyed to the higher depths of shade that necessitate the use of clearing since the original research used depths of shade only up to 2% o.m.f. In addition, some relationships between the effects of the treatments and specific features

of the molecular structure of the dyes have been developed. The efficiency of the wash-off treatment in the removal of superficial dye particles was assessed by measuring the absorbance of the acetone extract of the dyed samples, washfastness and rubfastness. The effect of the detergent based wash-off treatment on the colouristic properties of the dyed polyester was also determined.

4.6.1 Assessment of Surface Dye Removal after the Wash-off Treatment

The amount of the dye removed from the surface of the dyed samples was determined by measuring the absorbance of the acetone extract of the treated samples as described in Section 3.3.8. The concentration of the dye in the acetone extract was calculated from the absorbance and the measured extinction coefficients of the respective dyes. These values are given in Table 4.36. The percentage of the dye removed from the surface is shown in Figures 4.53 – 4.57 for dyes **1** – **5** respectively. It is observed from the figures that wash-off treatment is quite effective in the removal of surface deposits of dyes **1** and **2** as indicated by a high percentage of dye removed, in the ranges 85 – 95% and 75 – 85% for dyes **1** and **2** respectively. The detergent based wash-off treatment gives comparable results to reduction clearing with sodium dithionite in the case of dye **1** except at the 1% depth of shade where wash-off removes more of the surface dye.

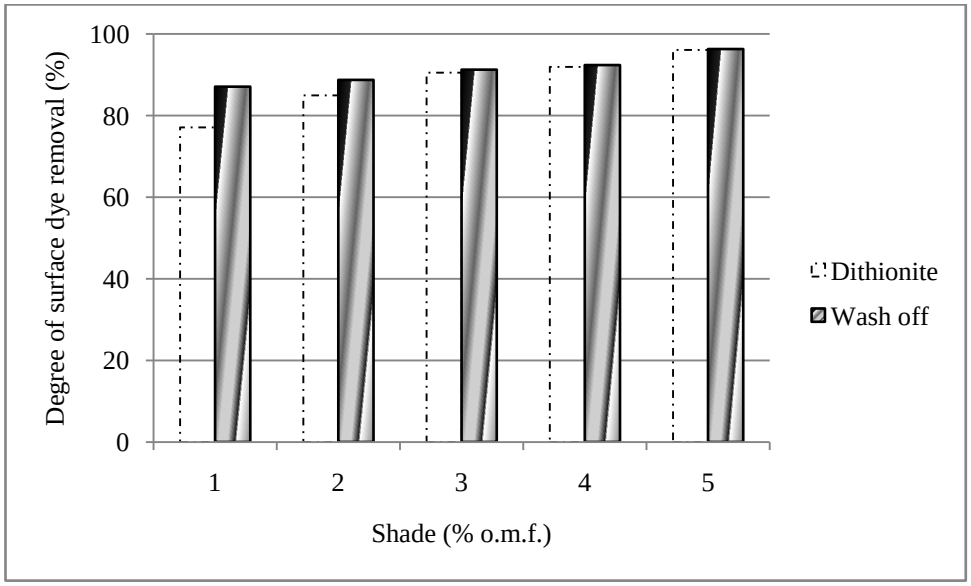


Figure 4.53 Degree of surface dye removal from samples dyed with dye **1** after reduction clearing and wash-off

Table 4.36 Concentration of dyes in the acetone extract of the dyed fabrics after reduction clearing with sodium dithionite and wash-off treatment

	Shade (%)	Untreated			Reduction cleared			Wash-off		
		λ_{max} (nm)	Abs.	Conc. (mg l^{-1})	λ_{max} (nm)	Abs.	Conc. (mg l^{-1})	λ_{max} (nm)	Abs.	Concen. (mg l^{-1})
Dye **1**	1	439	0.25	2.50	433	0.06	0.57	412	0.03	0.32
	2	439	0.55	5.52	437	0.08	0.83	407	0.06	0.62
	3	440	1.24	12.33	437	0.12	1.17	404	0.09	0.92
	4	440	1.58	15.81	438	0.13	1.28	404	0.12	1.21
	5	442	3.0	29.95	437	0.12	1.19	404	0.13	1.32
Dye **2**	1	511	0.42	5.02	510	0.05	0.60	515	0.09	1.10
	2	511	0.86	10.33	512	0.12	1.39	513	0.21	2.50
	3	510	1.86	22.43	509	0.15	1.79	514	0.36	4.30
	4	511	2.73	32.91	507	0.19	2.25	515	0.52	6.30
	5	511	5.49	66.24	509	0.28	3.40	514	0.84	10.20
Dye **3**	1	512	0.46	4.03	511	0.35	3.08	506	0.24	2.11
	2	512	1.17	10.25	510	0.73	6.40	506	0.53	4.66
	3	512	1.92	16.82	508	0.88	7.69	507	0.82	7.21
	4	511	3.59	31.46	509	1.69	14.81	509	1.34	11.78
	5	511	5.43	47.58	511	2.36	20.68	508	1.83	16.07
Dye **4**	1	631	0.15	1.96	628	0.07	0.88	629	0.11	1.44
	2	630	0.33	4.25	628	0.15	1.95	630	0.21	2.63
	3	630	0.62	7.93	629	0.20	2.54	630	0.40	5.10
	4	630	0.58	7.50	630	0.33	4.27	630	0.47	6.0
	5	630	0.89	11.40	630	0.75	9.57	630	0.76	9.71
Dye **5**	1	666	0.09	2.35	666	0.03	0.82	665	0.05	1.20
	2	666	0.22	5.38	665	0.04	0.91	666	0.10	2.62
	3	666	0.36	8.92	666	0.06	1.47	665	0.18	4.48
	4	665	0.48	11.96	665	0.08	1.94	665	0.26	6.50
	5	666	0.88	22.02	665	0.10	2.48	666	0.38	9.43

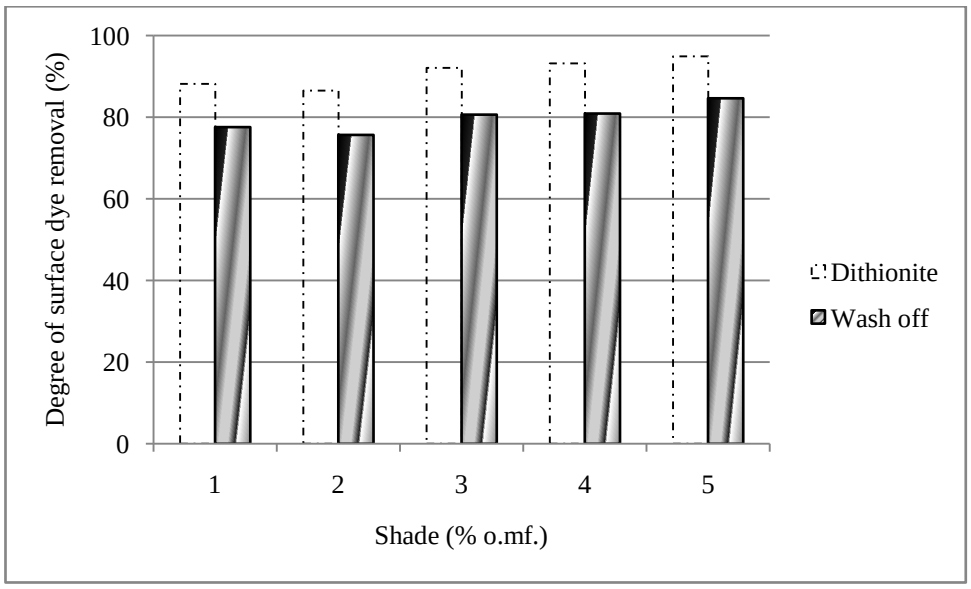


Figure 4.54 Degree of surface dye removal from samples dyed with dye **2** after reduction clearing and wash-off

In the case of samples dyed with dye **2** reduction clearing is slightly more efficient than wash-off and gives a consistently higher percentage of dye removal (85 – 95%) at all depths of shade (Figure 4.54). This feature may be explained in that the dye **2** has ester groups in the side chain which are potentially hydrolysed with alkali as discussed previously in Section 4.4.1. Detergent wash-off employs a weaker alkali, sodium carbonate, which may lead to a reduced amount of hydrolysis of the dye, and thus the lower level of dye removed from the surface of the dyed samples.

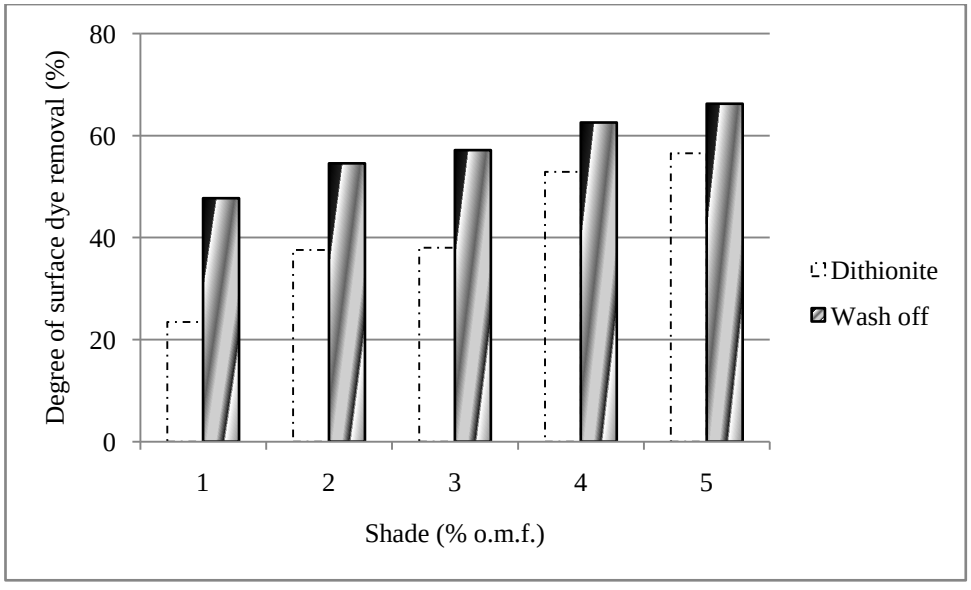


Figure 4.55 Degree of surface dye removal from samples dyed with dye **3** after reduction clearing and wash-off

Although, wash-off treatment is more effective than reduction clearing in the removal of surface deposits of dye **3**, the overall efficiency is significantly lower (45 – 65%) than was observed for dyes **1** and **2**, which gave 75 – 97% dye removal. However, the difference between the amounts of surface dye removed by reduction clearing and wash-off decreases at higher depths of shade (Figure 4.55).

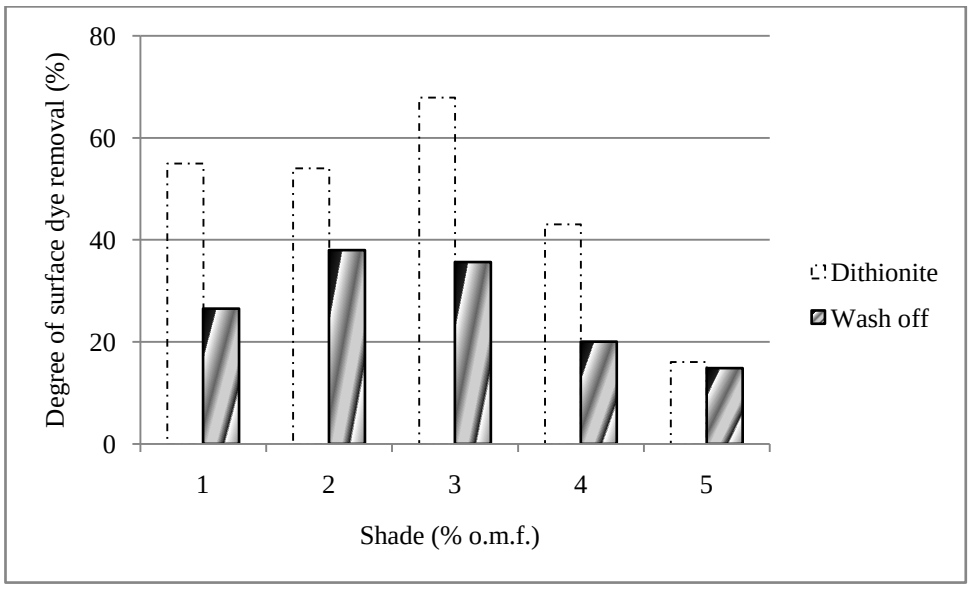


Figure 4.56 Degree of surface dye removal from samples dyed with dye **4** after reduction clearing and wash-off

In the case of dyes **4** and **5**, the detergent base wash-off is markedly less efficient than reduction clearing, giving a dye removal percentage of 15 - 40% for dye **4** and 45 – 60% for dye **5**, as illustrated in Figure 4.56 and Figure 4.57.

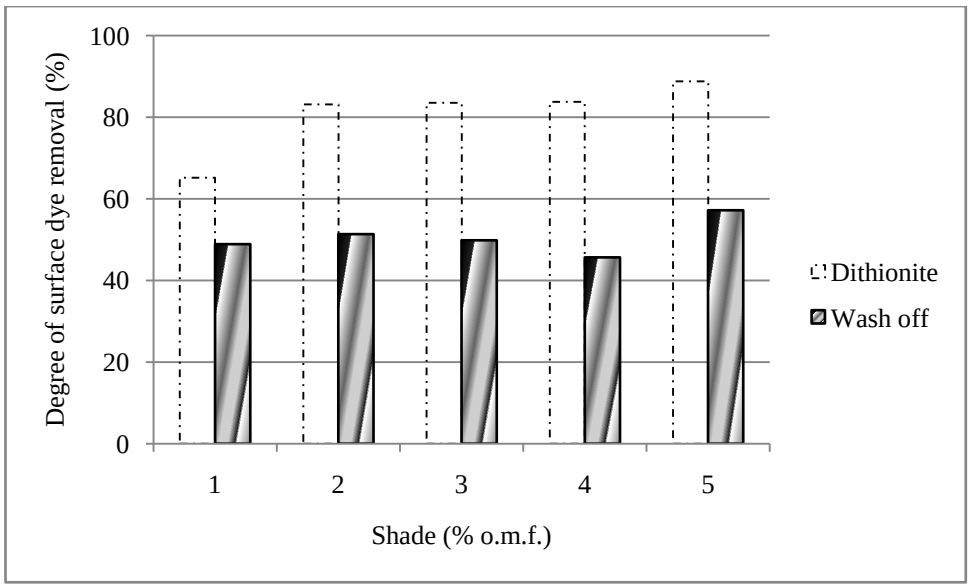


Figure 4.57 Degree of surface dye removal from samples dyed with dye **5** after reduction clearing and wash-off

Thus, a generalised statement may be made that the detergent based wash-off is not effective for the anthraquinone dyes while it is reasonably effective for the azo dyes. Whether this is a general feature of the dye classes would need to be verified by investigation of a wider range of dyes.

However, the general trend which has been commonly observed throughout these investigations of an increase in the percentage of dye removed with an increasing depth of shade is also observed for the wash-off treatment. Samples dyed with dye **4** show the opposite behaviour in this regard with the percentage of dye removed by wash-off decreasing at higher depths of shade. Such a trend was also observed after reduction clearing of samples dyed with dye **4** with sodium dithionite and hydroxyacetone. A possible explanation may be proposed that this particular dye becomes increasingly aggregated at the surface as the depth of shade increases and it becomes progressively more difficult to remove.

4.6.2 Washfastness Properties after the Wash-off Treatment

Generally speaking, the wash-off treatment fails to provide a significant improvement in the washfastness properties of the dyed polyester (Table 4.37). In the case of the three azo dyes, dyes **1**, **2** and **3**, wash-off treatment improves the stain rating by about one unit. However, for samples dyed with dye **4**, an anthraquinone dye, there is no improvement in washfastness properties at all. These results are in line with the percentage of surface dye removed, determined by the acetone extraction of the treated samples, as discussed in Section 4.6.1. It has been suggested that dye **4** contains four electron releasing groups (NH_2 and OH) which increase the electron density in the anthraquinone ring system, making it particularly resistant to reduction. There is no change in the washfastness properties of the samples dyed with dye **5** after the wash-off treatment. It was discussed in the previous sections for the organic and inorganic reducing agents (FAS/TUDO, hydroxyacetone, glucose and sodium dithionite), that dye **5** is not a good candidate for assessing the effectiveness of the clearing treatments because its washfastness properties are already excellent before clearing. Thus, the detergent based wash-off is more efficient in the case of azo dyes **1**-**3**, than anthraquinones **4** and **5** for the cases studied.

Table 4.37 Washfastness properties of the dyed samples after the wash-off treatment

		Shade (%)	Change in colour	Staining					
				Wool	Acrylic	PET	Nylon	Cotton	Acetate
Dye **1**	Untreated	1	5	5	5	5	4-5	5	5
		2	5	5	5	5	4-5	5	4-5
		3	5	5	5	5	4	5	4
		4	5	5	5	5	3-4	5	3-4
		5	5	4-5	5	4-5	3	5	3
	Washing-off	1	5	4-5	5	5	4-5	4-5	5
		2	5	4-5	5	5	4-5	4-5	4-5
		3	5	4-5	5	5	4-5	4-5	4-5
		4	5	4-5	5	5	4-5	4-5	4-5
		5	5	4-5	5	5	4-5	4-5	4-5
Dye **2**	Untreated	1	5	4-5	5	4-5	3-4	4-5	2-3
		2	5	4	4-5	3-4	3	4-5	2
		3	5	4	4-5	3	2-3	4-5	1-2
		4	4-5	3	4-5	2-3	2	4-5	1-2
		5	4-5	3	4-5	2-3	2	4	1-2
	Washing-off	1	5	5	5	5	4-5	5	4-5
		2	5	5	5	5	4	5	4
		3	5	5	5	4-5	3-4	5	3-4
		4	5	4-5	5	4-5	3	5	3
		5	5	4-5	5	4-5	2-3	5	2-3
Dye **3**	Untreated	1	5	4-5	5	4-5	4	5	3-4
		2	5	4-5	5	4	2-3	5	2-3
		3	4-5	4	5	3-4	2-3	5	2-3
		4	4-5	3-4	4-5	3	2	4-5	2
		5	4-5	3	4-5	3	1-2	4-5	1-2
	Washing-off	1	5	5	5	4-5	4-5	5	4-5
		2	4-5	5	5	4-5	3-4	5	3-4
		3	4-5	4-5	5	4-5	3	5	3
		4	4-5	4	4-5	4	2-3	4-5	3
		5	4-5	4	4-5	3-4	2-3	4-5	3

		Shade (%)	Change in colour	Staining					
				Wool	Acrylic	PET	Nylon	Cotton	Acetate
Dye **4**	Untreated	1	4-5	4-5	5	4-5	3-4	4-5	4-5
		2	4-5	4-5	5	4-5	3	4-5	4
		3	4-5	4	5	4	2-3	4-5	3-4
		4	4-5	4	4-5	4	2	4-5	3-4
		5	4-5	3-4	4-5	3-4	1-2	4-5	3
	Washing-off	1	4-5	4-5	5	4-5	3-4	5	4-5
		2	4-5	4	5	4-5	2-3	5	4
		3	5	4	5	4	2	4-5	3-4
		4	5	3-4	5	4	2	4-5	3
		5	5	3	5	3-4	1-2	4-5	2-3
Dye **5**	Untreated	1	4	4-5	5	5	5	5	5
		2	4-5	4-5	5	5	5	5	5
		3	4-5	4-5	5	5	5	5	5
		4	4-5	4-5	5	5	5	5	5
		5	4-5	4-5	5	5	5	5	5
	Washing-off	1	4-5	4-5	5	5	5	5	5
		2	4-5	4-5	5	5	5	5	5
		3	4-5	4-5	5	5	5	5	5
		4	4-5	4-5	5	5	5	5	5
		5	5	4-5	5	5	5	5	5

4.6.3 Rubfastness Properties after the Wash-off Treatment

The results of the rubfastness of the samples after the wash-off treatment are given in Table 4.38. The corresponding results for the untreated and reduction cleared samples are also provided for comparison. Wash-off treatment improves the rubfastness of all the samples to excellent as indicated by stain ratings of 4-5 and 5. It has been previously suggested that rubfastness properties appear to be less sensitive to the presence of surface dye and only act as a secondary indicator of the efficiency of clearing treatments among the selected dyes.

Table 4.38 Rubfastness properties of the dyed samples after the wash-off treatment

	Shade (%)	Dye **1**		Dye **2**		Dye **3**		Dye **4**		Dye **5**	
		Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Untreated	1	5	5	4-5	4-5	4-5	5	4-5	4-5	5	5
	2	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5	5
	3	4-5	4-5	4	4	4	4-5	4-5	4	5	5
	4	4	4-5	4	3-4	3-4	4	4-5	4	5	5
	5	3-4	4	3-4	3	3-4	4	3-4	3-4	5	5
Reduction cleared	1	5	5	5	5	5	5	5	5	5	5
	2	5	5	5	5	4-5	5	5	5	5	5
	3	5	5	5	5	4-5	5	5	5	5	5
	4	5	5	5	5	4-5	5	5	5	5	5
	5	5	5	5	5	5	5	5	4-5	5	5
Washing-off	1	5	5	5	5	5	5	5	5	5	5
	2	5	5	5	5	4-5	5	4-5	4-5	5	5
	3	5	5	5	5	4-5	5	4-5	4-5	5	5
	4	5	5	5	5	4-5	4-5	4-5	4-5	5	5
	5	5	5	5	5	4	4-5	4-5	4-5	5	5

4.6.4 Colour Properties after Wash-Off Treatment

The colour measurements of the samples dyed with dyes **1** - **5** after the wash-off treatment are given in Appendix (Table 6 – Table 10). The difference in the colour parameters of the dyed samples after the detergent wash-off treatment is given in Table 4.39.

In the case of azo dyes **1** - **3**, the overall colour difference values (ΔE) broadly increase with increasing depth of shade. However, this change is regular only for dye **3**. In the case of dye **4**, similar values are observed at all depths of shade while with dye **5** the colour differences decrease steadily with increasing depth of shade. This is a very similar pattern compared with the reduction clearing treatments and follows the tentative correlation with the chemical class of the dye, that is, generally, the clearing treatments produce higher colour differences in fabrics dyed with azo dyes as compared with those dyed with anthraquinone dyes. In terms of differences in lightness and chroma, the trends are also similar to those given by the reduction clearing processes.

Table 4.39 Differences in colour parameters after the washing-off treatment

	Shade (%)	ΔL*	Δa*	Δb*	ΔC*	ΔH*	ΔE (CMC)	Change in integ value
Dye **1**	1	0.65	-0.26	-0.13	-0.15	0.25	0.27	-1.33
	2	1.24	-0.13	1.3	1.27	0.31	0.61	-1.02
	3	0.97	0.24	1.07	1.09	-0.08	0.48	-0.79
	4	1.54	-0.19	2.0	1.93	0.54	0.86	-0.74
	5	0.82	0.32	0.7	0.75	-0.16	0.39	-0.95
Dye **2**	1	0.36	0.54	-0.78	0.47	-0.82	0.58	-0.95
	2	0.14	0.81	-0.6	0.71	-0.72	0.59	-0.33
	3	0.12	0.99	-0.55	0.86	-0.74	0.67	-0.23
	4	-0.05	0.77	-0.84	0.57	-0.99	0.82	-0.08
	5	-0.17	1.29	-0.82	1.06	-1.1	1.06	0.87
Dye **3**	1	-0.24	0.69	0.6	0.78	0.48	0.46	1.91
	2	-0.17	0.55	0.0	0.54	-0.13	0.28	1.48
	3	-0.15	0.34	0.15	0.29	-0.23	0.25	1.0
	4	0.17	1.24	-0.11	1.16	-0.44	0.69	-0.08
	5	0.04	1.21	-0.17	1.12	0.5	0.73	0.48
Dye **4**	1	-0.63	0.92	-0.83	0.82	0.92	0.87	1.2
	2	0.16	0.31	-1.0	1.03	0.18	0.52	0.35
	3	-0.03	0.43	-0.61	0.68	0.31	0.42	0.37
	4	0.11	0.25	-0.49	0.54	0.12	0.31	-0.26
	5	-0.47	0.46	-0.83	0.93	0.22	0.67	2.46
Dye **5**	1	1.02	1.45	-2.54	1.42	2.56	1.82	-0.38
	2	1.39	0.62	-1.56	1.12	1.25	1.16	-0.94
	3	1.15	0.54	-0.97	0.67	0.89	0.88	-1.12
	4	0.82	0.58	-0.75	0.53	0.79	0.74	-1.24
	5	0.51	0.52	-0.71	0.55	0.69	0.62	-0.78

In the case of fabrics dyed with dyes **1** and **5,** the wash-off treatment produces consistently lighter colours and no distinct relationship with the depth of shade. There are no specific trends in the lightness after the wash-off treatment of fabrics dyed with dyes **2**-**4**.

Virtually all samples show increased chroma after the detergent wash, the magnitude of most ΔC* values being significant. With dye **5**, the positive ΔC* values decrease

consistently with depth of shade but there was no distinct relationship observed with the other dyes. The effect of the detergent wash on hue is relatively small and broadly similar to the effect of the clearing processes. Comparatively, more significant and consistent effects are observed on the hue in the case of dyes **2, 4** and **5** than dyes **1** and **3**.

The effect on the integ values, a measure of colour strength, however, is different for the detergent wash compared with the reduction clearing processes. In the case of azo dyes **1, 2** and **5**, the integ values decrease after the detergent wash, implying a reduction in colour strength, the only exception being dye **2** at 5% depth of shade. With dye **3**, most integ values increase significantly, the difference in values decreasing with increasing depth of shade. The only other significant increases in integ value are given by dye **4** at 1% and 5%, but not at the intermediate depths of shade. This aftertreatment thus fails to provide the enhancement in the colour strength of the dyed fabrics which is provided by the reduction clearing in most, though not all, cases.

4.6.5 Scanning Electron Microscopy after Wash-off Treatment

Scanning electron micrographs of all the samples after the wash-off treatment are given in Figure 4.58 – Figure 4.62. All of the images show cleaner fibre surface, however, samples dyed with dyes **3**, **4** and **5** appear to have relatively more superficial particles (Figure 4.60, Figure 4.61 & Figure 4.62). These images are in line with the results of the acetone extraction of the treated samples as samples dyed with these three dyes gave a lower percentage of dye removal, less than 60% as shown in Figure 4.55, Figure 4.56 and Figure 4.57.

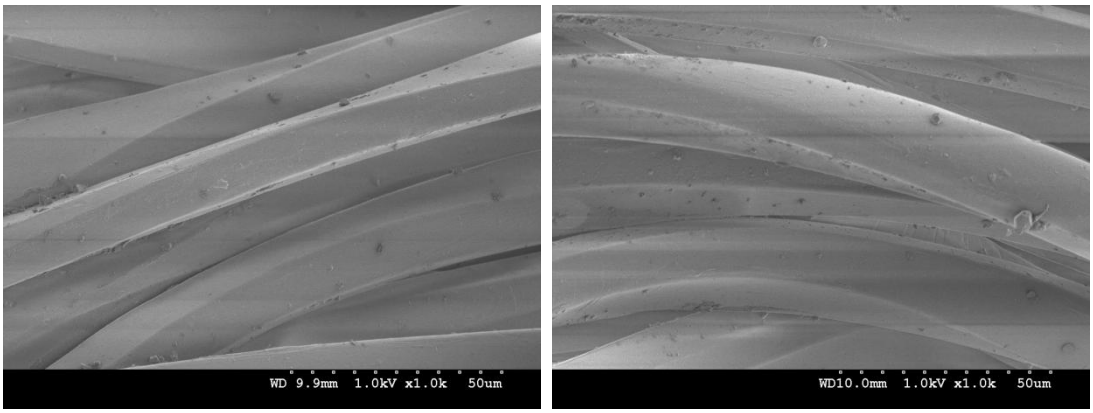


Figure 4.58 SEM images of samples dyed with dye **1** after wash-off treatment

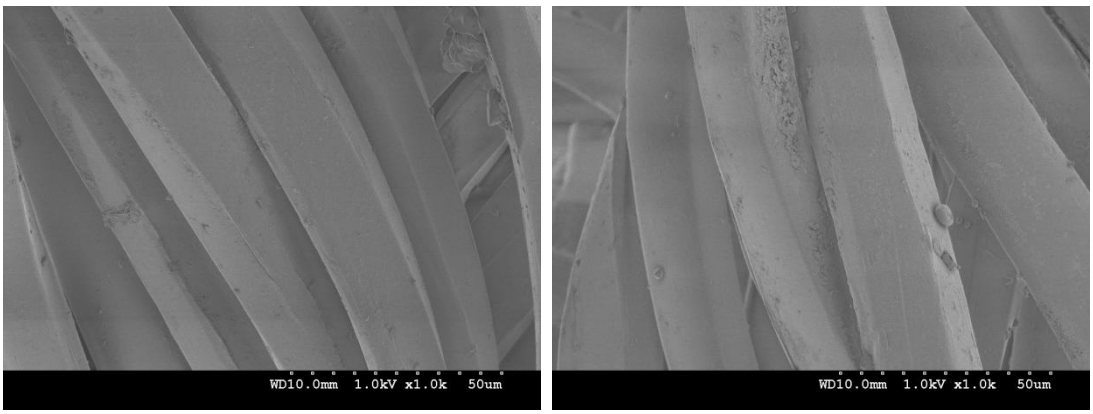


Figure 4.59 SEM images of samples dyed with dye **2** after wash-off treatment

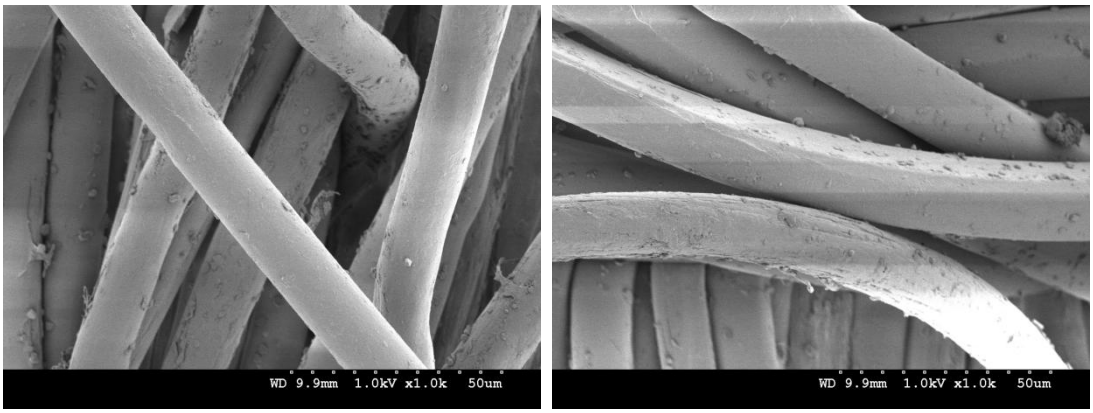


Figure 4.60 SEM images of samples dyed with dye **3** after wash-off treatment

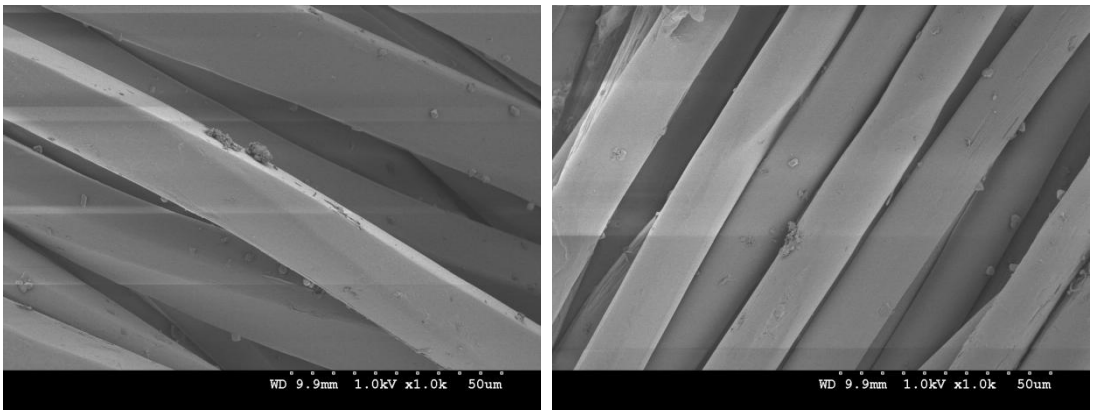


Figure 4.61 SEM images of samples dyed with dye **4** after wash-off treatment

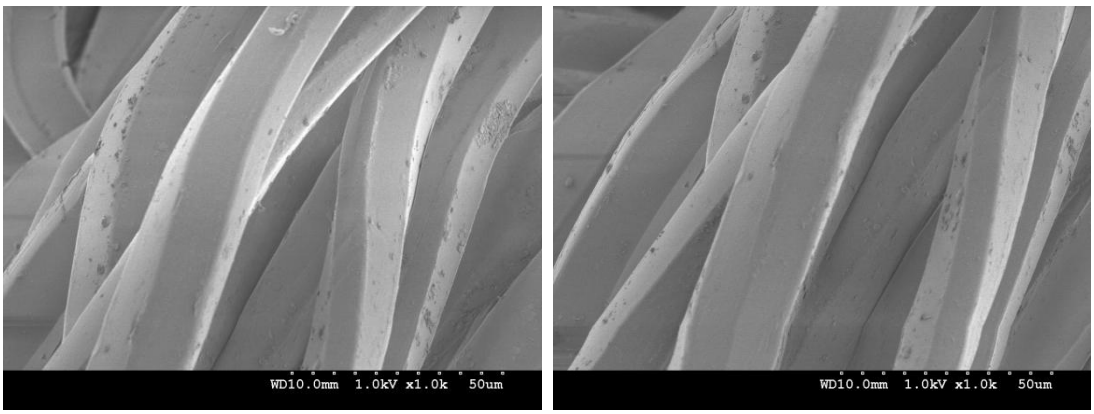


Figure 4.62 SEM images of samples dyed with dye **5** after wash-off treatment

4.7 Clearing with Enzymes

As discussed in Section 4.1, two enzymes belonging to different classes were selected in this research for the purpose of removing the surface dye from the dyed samples. One of the enzyme is a hydrolase and the other belongs to oxidase class. Reductive enzymes were not selected for this study because they require anaerobic conditions which poses limitations to their industrial application. NS 29076 was supplied by the manufacturers as an enzyme preparation and it was assayed to determine the enzyme activity. The laccase was a purified enzyme product and its activity was provided by the suppliers (Sigma Aldrich). The application conditions for clearing using the two types of enzymes were optimised one by one on the basis of the surface dye removal which was determined by the absorbance of the acetone extract of the samples dyed with dye **3** as described in Section 3.3.6. Initially, the effectiveness of clearing treatments was assessed by measuring the amount of surface dye removed as determined by the absorbance of the acetone extract of the treated samples. The rest of the samples were then treated using the optimised conditions and assessed further for the clearing efficiency by measuring the washfastness and rubfastness properties of the treated samples.

4.7.1 Determination of Esterase Activity

Enzymes are high molecular weight organic compounds which act as catalysts and thus are not consumed in reactions in which they participate. In contrast to other catalysts, only a small part of the entire three-dimensional structure of the enzyme, which is referred to as the active site, takes part in the catalytic reaction. Hence, the molecular mass of the enzymes does not provide an indication of its efficiency. Consequently, the efficiency of an enzyme is assessed by its effect on a chemical reaction to provide a value referred to as enzyme activity. The activity of an enzyme is measured based on

the formation of a product when a specific amount of enzyme catalyses a chemical reaction with a specific amount of substrate. Thus, for their variety of applications, activity is a useful parameter for the comparison of different enzymes and also for the determination of the required dosage.

NS29076 is an enzyme preparation, a sample of which was kindly provided by Novozymes, although its activity was not disclosed. As discussed in Section 2.8.5, the activity of an enzyme is an important property in the determination of the optimum conditions for application. Thus, the assay of the NS29076 enzyme was carried out to determine its activity. The activity was determined according to the Sigma quality control, enzymatic assay procedure for esterase [195]. However, *o*-nitrophenyl butyrate was replaced in the assay with *p*-nitrophenyl butyrate since the *o*-isomer was not available commercially. *p*-Nitrophenyl butyrate, which is an ester and thus an appropriate substrate for the esterase NS29076, is hydrolyzed to *p*-nitrophenol. In this reaction, the butyrate ester is colourless while the product, *p*-nitrophenol, is yellow. Hence, this reaction can be monitored spectrophotometrically. The rate of the formation of the product is used to calculate the activity of the enzyme by Equation 4.3.

$$\text{Units}/_{\text{ml}}\ \text{enzyme} = \frac{\left(\text{Change in absorbance of the test solution}, \Delta A/_{\text{time}}\right) \times 3 \times 100}{\text{millimolar extinction coefficient of p-nitrophenol} \times 0.1} \qquad (4.3)$$

Where 3 = Total volume of the assay (ml)

100 = dilution factor

0.1 = Volume of enzyme used (ml)

The change in absorbance over a period of about 15 minutes was measured by the UV/Vis spectrophotometer and the molar extinction coefficient of *p*-nitrophenol (PNP) was determined as described in Section 3.3.5. The absorbance was determined to be 3.1 at 420 nm and extinction coefficient was calculated to be 8.66 mmol l^{-1}. By substituting the values of molar extinction coefficient of PNP and the change in absorbance with time of the test solution in the Equation 4.3, the activity of the enzyme preparation NS29076 was calculated to be 17.59 U ml^{-1}.

4.7.2 Optimisation Experiments using NS29076

The optimization experiments were carried out for samples dyed with dye **3** at a 3% depth of shade only. A control experiment, consisting of only buffer and fabric, without enzyme was also carried out simultaneously with each of the trials. The results of the absorbance values of the experiments carried out in triplicate and control sample are given in Appendix (Table 4.11) while the average values are shown in Table 4.40.

Table 4.40 Absorbance values of the acetone extract of the samples dyed with dye **3** (3% o.m.f.) after clearing with NS29076 for optimisation experiments

Concentration of enzyme (ml l^{-1})	pH	Temperature (°C)	Time (hr)	Buffer	Absorbance
1	8	40	2	Citrate	1.27
1	8	40	4		0.78
1	8	40	5		1.44
1	8	40	6		0.93
1	8	40	16		1.32
1	8	40	20		1.11
1	8	40	24		0.85
1	8	40	2	Phosphate	0.89
1	8	40	4		0.91
1	8	40	1		1.11
1	8	40	0.5		1.31
2	8	40	2		0.93
5	5	60	2		0.86
10	5	60	2		0.78
1	8	50	2		1.26
1	8	60	2		0.93
1	5	60	2		0.75
1	9	60	2		1.1
1	5	40	2		1.23
1	5	70	2		0.83

The initial optimisation experiments for the clearing of dyed polyester with NS 29076 were carried out at pH 8 using a citrate buffer. However, as described in Section 3.3.5, this buffer showed poor stability when used to prepare the enzyme solution and did not give reproducible results. The buffer was then changed to phosphate which was used

for the rest of the optimization experiments. These optimization experiments were carried out at 40°C using an enzyme preparation concentration of 1 ml l^{-1}.

The assessment of the efficiency of the clearing effect was determined by measuring the absorbance of the acetone extract of the treated dyed fabric samples. The results given in Table 4.40 showed that increasing the time period of the treatment for longer than 2 hours did not lead to improvement in the surface dye removal. Thus, the rest of the experiments were carried out for a time period of 2 hours. In the second set of experiments, the concentration of the enzyme was increased to 2 ml l^{-1}. However, the extract absorbance value obtained at this concentration was not significantly different from the absorbance value obtained at a concentration of 1 ml l^{-1}. Thus, a concentration of 1 ml l^{-1} of NS29076 was considered as the optimum. After that, the temperature of the treatment was increased to 50°C and 60°C. Considering the absorbance values obtained at 40°C, 50°C and 60°C, the optimum temperature was finalized as 60°C. Finally, the influence of the pH of the treatment liquor at values of 5 and 9 was investigated. The lowest extract absorbance value was obtained at pH 5, indicating that the clearing effect of NS29076 is more efficient at pH 5. The concentration of the enzyme was then again varied using these new conditions. Experiments were carried out at enzyme concentrations of 5 ml l^{-1} and 10 ml l^{-1}. Since there was not a significant difference in the absorbance values obtained at these concentrations, washfastness tests were carried out to assess the influence of increasing the enzyme concentration. However, there was no significant change in the absorbance values or the washfastness results at these higher concentrations. The results of the washfastness tests are given in Table 4.12 in Appendix. Thus the optimum conditions for clearing with NS29076 were established as 2 ml l^{-1} enzyme preparation, at 60°C and pH 5.0 for 2 hours.

4.7.3 Assessment of Surface Dye Removal after Clearing with NS29076

The samples dyed with the five dyes at 3% depth of shade were treated with NS29076 using the optimised conditions. The experiments were carried out in triplicate as is common practice with enzyme processes to monitor reproducibility and improve accuracy. The absorbance values of the acetone extracts from the dyed and treated fabrics as well as the corresponding control trials are given in Table 4.41. The average of the three values was used to calculate the concentration of dye in the acetone extract.

Table 4.41 Amount of dyes in the acetone extract of the dyed samples after treatment with NS29076 at 60°C

		Sample1		Sample2		Sample 3		Average	
		λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	Abs.	Conc. (mg l^{-1})
Dye **1**	Control	440	0.81	440	0.88	440	0.83	0.84	8.40
	NS29076	439	0.46	440	0.62	440	0.52	0.54	5.35
Dye **2**	Control	510	1.27	511	1.26	511	1.19	1.24	15
	NS29076	518	0.74	519	0.65	519	0.70	0.70	8.39
Dye **3**	Control	511	1.22	511	1.214	511	1.32	1.25	10.96
	NS29076	511	0.87	511	0.7	511	0.67	0.74	6.53
Dye **4**	Control	629	0.27	630	0.31	630	0.28	0.29	3.68
	NS29076	630	0.13	629	0.17	631	0.20	0.17	2.16
Dye **5**	Control	665	0.23	666	0.24	665	0.2	0.23	5.64
	NS29076	667	0.19	665	0.18	665	0.21	0.19	4.84

The average values are tabulated in Table 4.42 and shown graphically in Figure 4.63, in comparison with the results of reduction clearing with sodium dithionite. The results show that NS29076 removes significantly less surface dye than sodium dithionite in the case of dyes **1**, **2** and **5**. However, the efficiency of NS29076 in the case of dyes **3** and **4** is comparable, in fact slightly higher than reduction clearing with sodium dithionite (Figure 4.64).

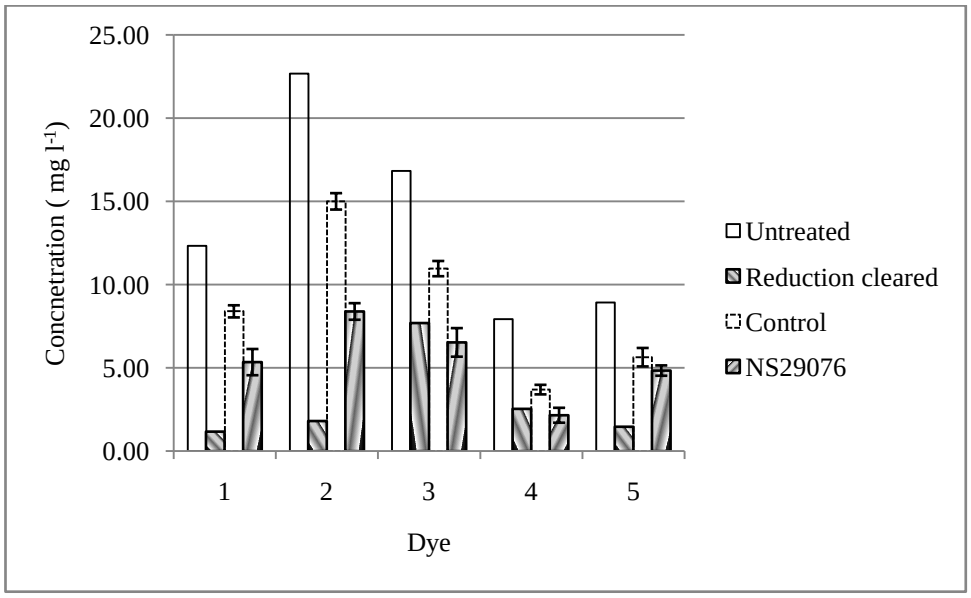


Figure 4.63 Concentration of dyes in the acetone extract of the dyed samples after reduction clearing with sodium dithionite and treatment with NS29076

Table 4.42 Concentration (mg l^{-1}) of dyes in the acetone extract of the dyed samples after reduction clearing with sodium dithionite and treatment with NS29076

	Untreated	Reduction cleared	Control	NS29076
Dye**1**	12.33	1.17	8.4	5.35
Dye **2**	22.67	1.81	15	8.39
Dye **3**	16.82	7.69	10.96	6.53
Dye **4**	7.92	2.54	3.7	2.16
Dye **5**	8.92	1.47	5.64	4.84

The percentage of surface dye removed after treatment with NS29076 for dyes **2** and **3** is similar, 63% and 61% respectively, as illustrated in Figure 4.64. However, the difference between the dye removed by reduction clearing and using NS29076 is greater for dye **2** than for dye **3**. In fact, treatment of samples dyed with dye **3** with NS29076 removes slightly more dye (61%) than reduction clearing with sodium dithionite (54%).

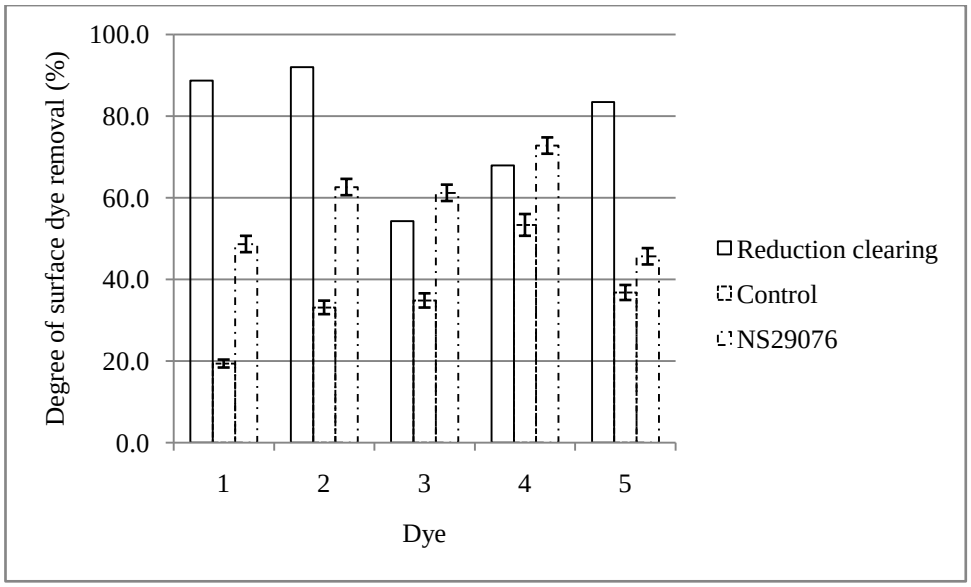


Figure 4.64 Degree of surface dye removal after reduction clearing with sodium dithionite and treatment with NS29076

Treatment with NS29076 is most effective for the samples dyed with dye **4** giving a percentage dye removal of 73%. A possible explanation for a higher efficiency of NS29076 in this case may be proposed in that this particular dye has a greater tendency to form aggregates on the fibre surface. Since NS29076 belongs to carboxyl esterase class of enzymes, it has the potential to hydrolyse the ester linkages of polyester superficially. This may facilitate the removal of the aggregated dye particles from the

hydrolysed fibre surface. This results in relatively easier removal of dye aggregates present on the fibre surface as compared to reduction with sodium dithionite.

In the case of dye **2**, experiments were also carried out at pH 8 and 9 in addition to the optimum pH 5 which was determined experimentally for dye **3.** These experiments were carried out to investigate the potential effects on the ester group of dye **2**, which is potentially hydrolysable by alkali as well as by the esterase activity of the enzyme, on reaction with NS29076 in alkaline medium. A comparison of the concentration of dye **2** in the acetone extract after treatment with NS29076 at various pH values is given in Table 4.43. The results show that the maximum amount of surface dye is removed under the acidic conditions at pH 5. As the alkalinity of the medium is increased, the dye removal decreases. An explanation may be proposed that the esterase catalyses the hydrolysis of the ester group in dye **2** more efficiently at pH 5 than at alkaline pH. At pH 9, the concentration of dye **2** in the extract of the cleared sample is higher than the control sample indicating that the sample treated with enzyme has a higher amount of surface dye than the control sample. It is possible that pH 9 provides sufficient alkalinity to remove some of the dye without the addition of any other agent. An alternative explanation may be that the enzyme becomes unstable at alkaline pH and thus less dye is removed in the presence of enzyme.

Table 4.43 Amount of dye **2** in the acetone extract of the treated samples after treatment with NS29076 at various pH values

pH		Sample1		Sample2		Sample 3		Average	
		λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	Abs.	Conc. (mg l^{-1})
5	Control	510	1.27	511	1.26	511	1.19	1.2	15
	NS29076	518	0.74	519	0.65	519	0.70	0.70	8.39
8	Control	512	1.14	511	1.23	510	1.38	1.25	15.08
	NS29076	512	0.85	512	1.08	512	1.03	0.99	11.92
9	Control	511	0.98	511	1.05	511	0.94	0.99	11.96
	NS29076	512	1.11	513	0.97	512	1.0	1.03	12.42

The treatment of the dyed samples with NS29076 was also carried out at 70°C to provide a more direct comparison with sodium dithionite, although it was not clear if the enzyme would be stable at this temperature. The rest of the conditions were the same as were used at 60°C. The results of the experiments are given in Table 4.44.

Table 4.44 Amount of dyes in the acetone extract of the dyed samples after treatment with NS29076 at 70°C

		Sample1		Sample 2		Sample 3		Average	
		λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	λ_{max} (nm)	Abs.	Abs.	Conc. (mg l^{-1})
Dye **1**	Control	440	0.92	440	0.85	440	0.90	0.89	8.88
	NS29076	440	0.38	440	0.40	440	0.39	0.39	3.92
Dye **2**	Control	511	1.09	511	0.90	510	0.99	0.99	11.96
	NS29076	517	0.69	518	0.50	517	0.33	0.50	6.08
Dye **3**	Control	511	1.16	510	1.07	511	1.28	1.17	10.26
	NS29076	511	0.85	511	0.77	511	0.86	0.83	7.25
Dye **4**	Control	631	0.23	631	0.20	630	0.24	0.23	2.90
	NS29076	630	0.21	631	0.18	631	0.18	0.19	2.45
Dye **5**	Control	666	0.22	664	0.22	665	0.22	0.22	5.53
	NS29076	664	0.14	665	0.14	666	0.15	0.14	3.60

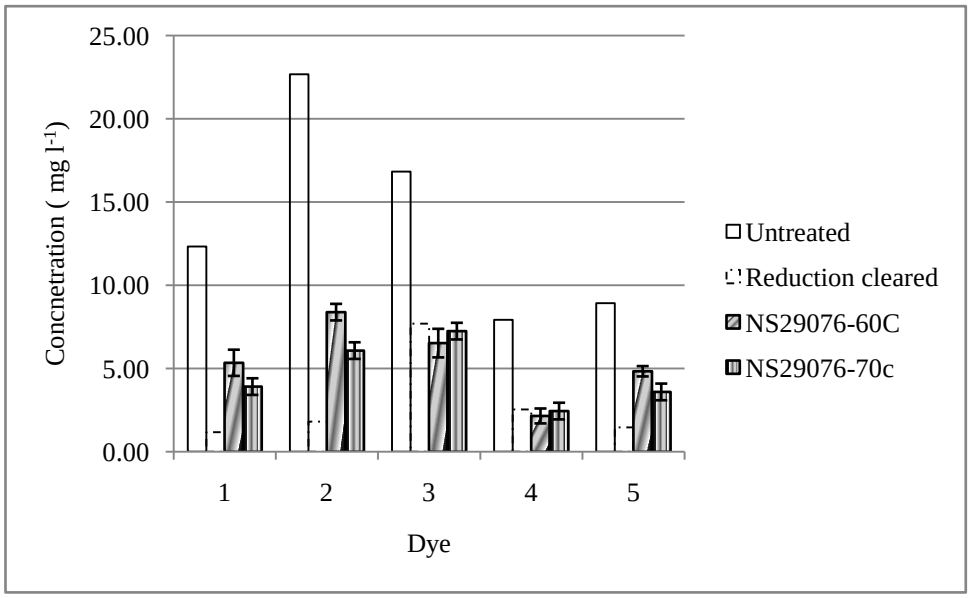


Figure 4.65 Comparison of the concentration of dyes in acetone extract of the dyed samples after treatment with NS29076 at 60°C and 70°C

A comparison of the concentration of dyes in the acetone extract after treatment with NS29076 at 60°C and 70°C is shown graphically in Figure 4.65 and the percentage of surface dye removed is shown in Figure 4.66.

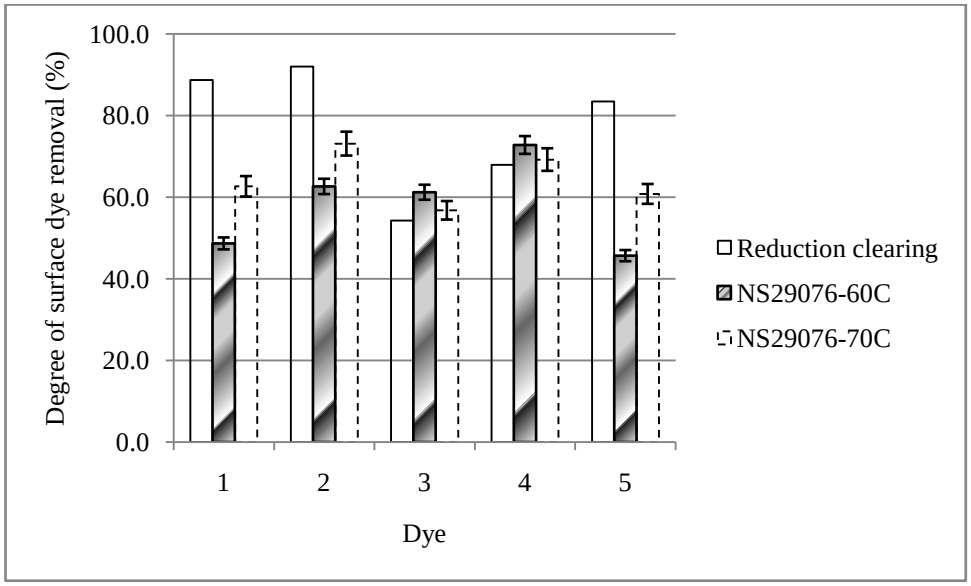


Figure 4.66 Degree of surface dye removal after reduction clearing with sodium dithionite and treatment with NS29076

It is observed that the treatment at the higher temperature results in a lower concentration of dye in the acetone extract for dyes **1**, **2** and **5** thus indicating higher efficiency of clearing. This is in line with the general principles of chemical reactions, whereby an increase in temperature leads to a corresponding increase in the rate of chemical reaction. However, in the case of dyes **3** and **4**, an increase in temperature does not lead to a higher removal of surface dye in clearing. In contrast, at the higher temperature the amount of surface dye removed decreases for these two dyes as indicated by a higher concentration of dye in the acetone extract (Figure 4.65). Nevertheless, it may be inferred from the results that NS29076 is stable at temperatures of 70°C as three of the dyes show improved removal of surface dye at this temperature. The decrease in the removal of surface dye at higher temperature for dyes **3** and **4** may be due to specific features of these particular dyes. Both dyes **3** and **4** also exhibited irregular behaviour after reduction clearing with sodium dithionite and responded poorly to reduction when compared with the rest of the dyes. This difference in the behaviour of these two dyes cannot be ascribed to a specific chromophoric group as dye **3** is azo while dye **4** has an anthraquinone structure. Although dyes **2** and **3** both possess an azo chromophore, their behaviour does not match. Similarly, dye **5** is an anthraquinone but behaves differently from dye **4** which is also an anthraquinone. It is proposed that the difference in the behaviour of dyes **2** and **3** arises from the presence of ester group in dye **2** which renders it susceptible to hydrolysis either by alkali or

catalysed by the enzyme. However, since enzymes are substrate specific, it may be that dyes **3** and **4** interact with the enzyme in a way that hinders its action at high temperature.

4.7.4 Washfastness Properties after Treatment with NS29076

The results discussed in Section 4.4.2 have shown that the reduction clearing treatments do not produce a significant change in the colour of the dyed sample after the washfastness tests and that staining on nylon and acetate is the most distinctive parameter for the assessment of washfastness properties. Consequently, only the results of staining after the washfastness test are reported here. All the dyed samples were treated with NS29076 at 60°C as well as at 70°C. Initially, the washfastness of samples dyed with dye **3** after treatment with NS29076 at both 60°C and 70°C was determined. However, there was no significant improvement in the washfastness properties when the treatment was carried out at the higher temperature (Table 4.13, Appendix). Thus the washfastness of the rest of the samples treated at 70°C with NS29076 was not determined.

Table 4.45 Washfastness properties of the dyed samples after treatment with NS29076 at 60°C

		Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
Dye **1**	Untreated	5	5	5	4	5	4
	Reduction Cleared	5	5	5	5	5	5
	NS29076	4-5	5	5	3-4	5	3-4
Dye **2**	Untreated	4	4-5	3	2-3	4-5	1-2
	Reduction Cleared	5	5	5	5	5	4-5
	NS29076	3-4	5	4	2	4-5	2
Dye **3**	Untreated	4	5	3-4	2-3	5	2-3
	Reduction Cleared	4	4-5	4	2-3	5	3
	NS29076	3-4	4-5	3	2	5	2
Dye **4**	Untreated	4	5	4	2-3	4-5	3-4
	Reduction Cleared	4-5	5	4-5	3-4	5	4-5
	NS29076	3-4	5	4	2-3	4-5	3-4
Dye **5**	Untreated	4-5	5	5	5	5	5
	Reduction Cleared	5	5	5	5	5	5
	NS29076	4-5	5	5	3-4	5	3-4

In most of the cases, treatment with NS29076 at 60°C does not provide an improvement in the washfastness properties (Table 4.45). In some instances, there is a slight decrease in the washfastness rating, for example staining of dyes **1**, **3** and **5** on acetate and staining of dyes **1**, **2**, **3** and **5** on nylon. Samples dyed with dye **5** which generally exhibit excellent washfastness properties, show quite erratic behaviour after treatment with NS29076, as the staining on nylon and acetate increases which decreases the rating by about 1 unit. A similar decrease in rating was also observed after reduction clearing of samples dyed with dye **5** with glucose. However, the staining produced after treatment with NS29076 was red in colour while that after reduction clearing with glucose was blue. It is suggested that the dye degradation products formed after treatment with NS29076 have a different colour and are easily taken up by nylon. It is interesting to note that NS29076 is a cutinase and may be expected to hydrolyse ester groups. Nevertheless, in this study, it appears to have the ability to affect other dyes which do not have ester functionality. Another plausible reason for the increase in staining after treatment with NS29076 may be that the surface layer of fibre, where the dye particles are deposited and which is only loosened during the enzyme treatment, is removed during washfastness test because of the mechanical agitation provided during the test. As the dye particles are removed along with the superficial fibre layer, the possibility of the staining of the adjacent fibre increases, thus resulting in an apparent decrease in the washfastness properties.

4.7.5 Rubfastness Properties after Treatment with NS29076

A trend similar to washfastness properties is observed in the rubfastness properties of the dyed samples after treatment with NS29076 at 60°C as shown in Table 4.46. Generally, treatment with NS29076 does not produce any significant improvement in the rubfastness properties; however, there are slight improvements in the case of dyes **1**, **2** and **4**. Interestingly there is no decrease of the rubfastness properties of dye **5** after treatment with NS29076. However, both dry and wet rubfastness of dye **3** decrease slightly after treatment with NS29076. In most of the cases, there is no change in wet rubfastness of the dyed samples after treatment with NS29076 while dry rubfastness is improved slightly. This observation also favours the proposal made in the Section 4.7.4 about the decrease in washfastness properties after the treatment with NS29076. Since there is comparatively less mechanical agitation during the rubfastness test, the rubfastness properties are not deteriorated after enzyme treatment.

Table 4.46 Rubfastness of the dyed samples after treatment with NS29076 at 60°C

		Dry	Wet
Dye **1**	Untreated	4-5	4-5
	Reduction Cleared	5	5
	NS29076	5	4-5
Dye **2**	Untreated	4	4
	Reduction Cleared	5	5
	NS29076	5	4
Dye **3**	Untreated	4	4-5
	Reduction Cleared	4-5	5
	NS29076	3-4	4
Dye **4**	Untreated	4-5	4
	Reduction Cleared	5	5
	NS29076	5	4
Dye **5**	Untreated	5	5
	Reduction Cleared	5	5
	NS29076	5	5

4.7.6 Colour Properties after Treatment with NS29076

The colour properties of the dyed samples after treatment with cutinase NS29076 at 60°C are given in Table 4.47. The lightness, as indicated by L* value, of all the dyes after treatment with NS29076 generally follows the same trend as was observed after reduction clearing with sodium dithionite (Table 4.14). The only exception is observed in the case of samples dyed with dye **1** whose lightness behaves in a manner opposite to that after reduction clearing with sodium dithionite. Since the numerical values of less than 0.5 may be interpreted as showing a visually imperceptible colour difference, the only significant change in lightness is observed for the samples dyed with dyes **1** and **2**. In both the cases, treatment with NS29076 results in a decrease in lightness, or negative ΔL* values. Samples dyed with dye **3** also exhibit a decrease in lightness, although the values are insignificant, whereas the lightness of samples dyed with dye **4** increases and there is no change in lightness (ΔL* is zero) of samples dyed with dye **5**.

Table 4.47 Colour properties of the dyed samples after treatment with NS29076 at 60°C

Sample		L*	a*	b*	C*	h°	Integ value	ΔL*	Δa*	Δb*	ΔC*	ΔH*	ΔE (CMC)	Change in integ value
Dye **1**	Untreated	78.62	17.67	102.31	103.83	80.2	27.83							
	Sodium dithionite	79.78	18.08	104.66	106.21	80.2	28.59	1.16	0.41	2.35	2.38	-0.01	0.81	0.76
	NS29076	76.66	17.56	99.26	100.8	79.97	28.22	-1.96	-0.11	-3.06	-3.03	-0.42	1.16	0.39
Dye **2**	Untreated	24.59	34.05	7.14	34.79	11.84	47.58							
	Sodium dithionite	24.4	34.94	6.76	35.59	10.95	48.9	-0.19	0.89	-0.38	0.8	-0.51	0.56	1.32
	NS29076	24.11	34.18	7.06	34.9	11.67	49.93	-0.49	0.12	-0.08	0.11	-0.1	0.36	2.35
Dye **3**	Untreated	23.27	32.12	8.5	33.23	14.82	53.79							
	Sodium dithionite	23.13	32.91	8.29	33.93	14.14	54.98	-0.14	0.78	-0.21	0.71	-0.4	0.46	2.75
	NS29076	23.15	32.39	8.45	33.47	14.61	54.62	-0.12	0.26	-0.05	0.24	-0.12	0.17	0.83
Dye **4**	Untreated	22.18	6.21	-30.07	30.7	281.68	38.83							
	Sodium dithionite	22.44	6.36	-30.55	31.21	281.77	38.18	0.26	0.15	-0.48	0.5	0.05	0.32	-0.65
	NS29076	22.48	6.04	-30.3	30.89	281.27	38.1	0.3	-0.18	-0.23	0.19	-0.22	0.32	-0.73
Dye **5**	Untreated	40.82	-13.57	-33.99	36.6	248.24	15.8							
	Sodium dithionite	40.88	-12.56	-35.18	37.35	250.35	15.78	0.06	1.01	-1.18	0.75	1.37	0.98	-0.02
	NS29076	40.83	-13.33	-33.67	36.21	248.4	15.47	0	0.24	0.33	-0.39	0.1	0.19	-0.33

The change in chroma after treatment with NS29076 is significant only for samples dyed with dye **1** (ΔC* greater than 0.5). The rest of the dyed samples show only a small change in chroma after treatment with NS29076. The chroma of the samples dyed with dyes **2**, **3** and **4** increases after treatment with NS29076 while the chroma of samples dyed with dyes **1** and **5** decreases after treatment with NS29076. Thus, if enhanced brightness is indicated by a positive ΔC* value, samples dyed with dyes **2**, **3** and **4** are slightly brighter after treatment with NS29076 while the samples dyed with dyes **1** and **5** become duller after treatment with NS29076, although only dye **1** may be considered as becoming perceptibly duller. The changes in hue for all the dyed samples after treatment with NS29076 are also insignificant and generally follow the same trend as were observed after reduction clearing with sodium dithionite (Table 4.14).

The overall colour difference represented by ΔE(CMC) are smaller than after reduction clearing with sodium dithionite except for samples dyed with dye **1**. The colour properties of samples dyed with dye **1** are unusual in that they are not in line with the general trends which are shown by other dyes. Interestingly, the change in integ value of samples dyed with dye **1** is quite small compared with the rest of the dyes. The integ value of all the dyes increases after treatment with NS29076 indicating an increase in the colour strength of the treated samples. However, two exceptional cases are observed for the samples dyed with dyes **4** and **5**, in which case, integ values decrease after the treatment with enzyme indicating a decrease in colour strength. Nevertheless, the integ values of all the dyed samples after treatment with NS29076 shows a similar trend as were observed after reduction clearing with sodium dithionite. The change in integ value after treatment with NS29076 of samples dyed with dye **2** is greater than after reduction clearing with sodium dithionite whereas dye **3** exhibits an opposite trend with reduction clearing producing a greater change in integ value. Thus, in general there are no specific trends in the colour properties after treatment with NS29076. It is interesting to note that despite the differences in the measured level of the removal of surface dye, both reduction clearing and treatment with NS29076 produce similar changes in the colouristic properties of the dyed samples in most of the cases.

4.7.7 Scanning Electron Microscopy after Treatment with NS29076

The scanning electron microscopic images of all the dyed samples (3% o.m.f) after treatment with NS29076 are shown in Figure 4.67 - Figure 4.71. A comparison of with the images of the respective dyed samples (Figure 4.8, Figure 4.10, Figure 4.12, Figure 4.14, Figure 4.16) shows that the enzyme treated samples are relatively cleaner and show a reduced number of superficial particles. Although the differences are not large, they are in line with the results of the acetone extraction and washfastness tests.

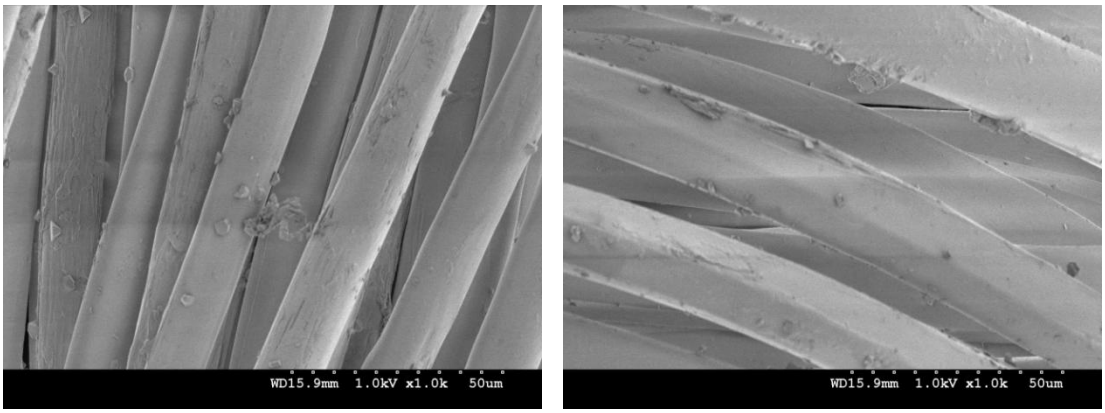


Figure 4.67 SEM images of samples dyed with dye **1** after treatment with NS29076

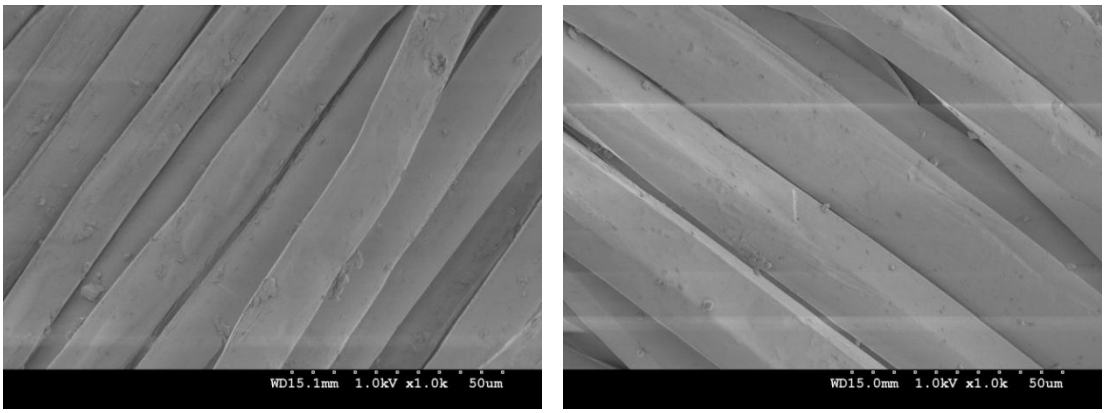


Figure 4.68 SEM images of samples dyed with dye **2** after treatment with NS29076

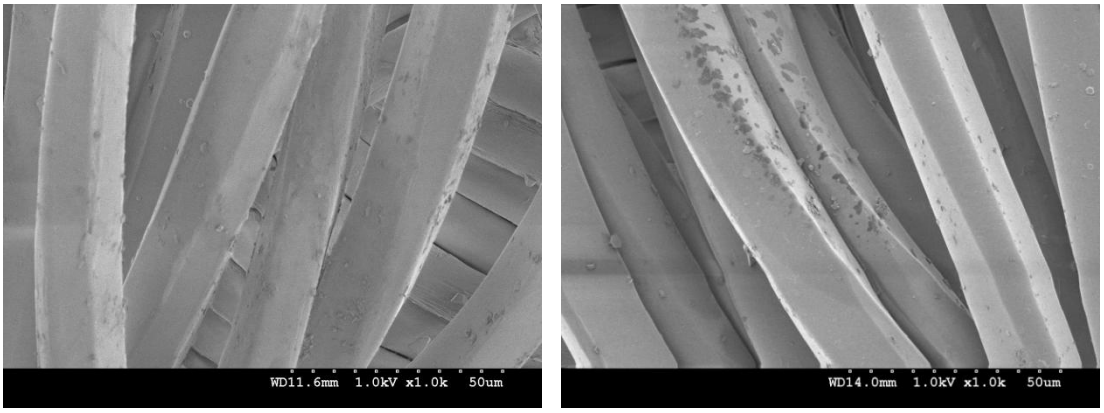


Figure 4.69 SEM images of samples dyed with dye **3** after treatment with NS29076

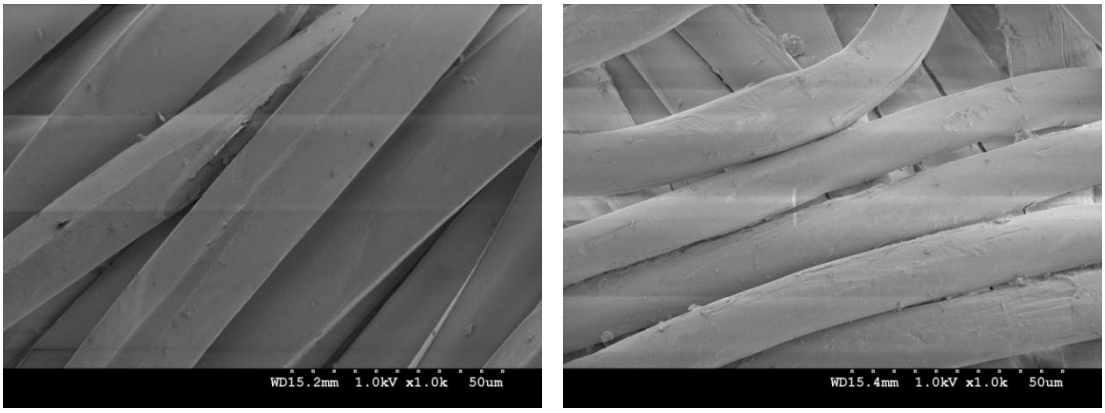


Figure 4.70 SEM images of samples dyed with dye **4** after treatment with NS29076

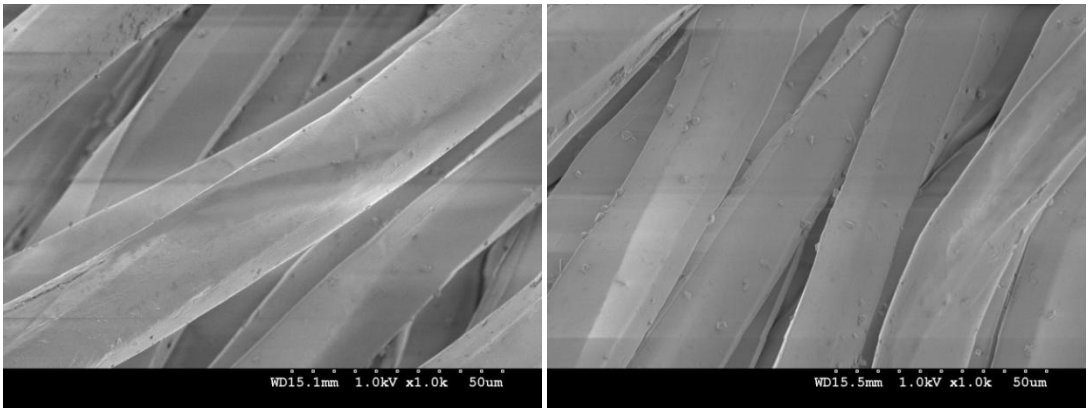


Figure 4.71 SEM images of samples dyed with dye **5** after treatment with NS29076

4.7.8 Optimization Experiments using a Laccase Derived from Trametes versicolor

A series of optimization experiments on the clearing of dyed polyester with laccase were performed for samples dyed with dye **3** at a depth of shade of 3% o.m.f. The range of these optimisation experiments is shown in Table 4.48.

Table 4.48 Range of experiments for the optimisation of conditions for the treatment of samples dyed with dye **3** (3% o.m.f) with a laccase from *Trametes versicolor*

Laccase (x 10^3 U l^{-1})	HBT (mM l^{-1})	pH	Temp (°C)	Time (hr)	Absorbance
1	1	5	30	48	0.73
1	1	5	30	40	0.68
1	1	5	30	28	0.78
1	0	5	30	24	1.69
1	1	5	30	24	0.96
1	1	5	30	20	0.74
1	1	5	30	18	0.71
1	1	5	30	14	0.74
1	1	5	30	8	0.81
1	1	5	30	7	0.71
1	1	5	30	4	0.84
1	1	5	30	2	0.85
1	1	5	30	1	0.97
1	0.5	5	30	2	1.19
1	2	5	30	2	0.97
1	5	5	30	2	0.9
1	1	5	25	2	1.08
1	1	5	40	2	0.71
1	1	5	50	2	0.72
1	1	3	40	2	1.25
1	1	7	40	2	1.43
0.5	1	5	40	2	0.9
1.5	1	5	40	2	0.68
2	1	5	40	2	0.78

The first experiment was carried out to investigate the influence of the commonly-used mediator 1-hydroxybenzotriazole (HBT) on the treatment of dyed fabric with laccase. It was carried out together with two control experiments, one without enzyme and mediator and one with mediator but without enzyme. Initially, a temperature of 30°C at pH 5 with a concentration of 1000 U l^{-1} enzyme was used for a time period of 24 hours. The efficiency of clearing was determined by measuring the absorbance of the acetone extract of the treated samples. The absorbance value of the samples treated with enzyme in the presence of 1-hydroxybenzotriazole (0.96) was significantly lower than the samples treated with enzyme only (1.69). Comparison with the absorbance of the extracts from the untreated samples (1.92, Table 4.2) indicates that laccase is effective only in the presence of mediator and had almost no clearing effect in its absence. Thus, all of the subsequent experiments with laccase were carried out in the presence of 1-hydroxybenzotriazole.

The experiments were carried out in triplicate and a control experiment was performed simultaneously with each test. The next stage in the experimentation was carried out to optimize the time period for the treatment. A series of experiments for various time periods which ranged from 1 to 48 hours was carried out as shown in the Table 4.48. The table only shows the average of the triplicate experiments. The data for the triplicate trials is given in Table 14 in the Appendix. These were all carried out at a pH of 5, temperature 30°C, with a concentration of 1000 U l^{-1} laccase in the presence of 1 mM l^{-1} 1-hydroxybenzotriazole (HBT). An inspection of the corresponding absorbance values (Table 4.48) reveals that there is no significant decrease in the absorbance values when carried out for longer periods of time. Hence, a time period of 2 hours for the treatment of dyed fabric with laccase was considered to be the optimum and this was used for all of the subsequent experiments. After the time optimization, experiments were then carried out using various concentrations of HBT to investigate its optimum value. HBT was used at concentrations of 0.5, 1, 2 and 5 mM l^{-1} in this set of experiments. At a lower concentration of HBT (0.5 mM l^{-1}), the value of the absorbance increased (1.19) while at concentrations of 1 and 2 mM l^{-1}, the absorbance value remained the same (0.97) and at the highest concentration of 5 mM l^{-1}, there was only a marginal decrease in the absorbance value (0.90). Consequently, a concentration of 1 mM l^{-1} HBT was considered to be the optimum for the treatment of dyed fabric with laccase. In the next stage, experiments were devised to investigate the influence of temperature on the laccase treatment. Laccase was used at

temperatures of 25, 30, 40 and 50°C under conditions which had been optimized so far (2 hours, 1 mM l^{-1} HBT). An absorbance value of 1.08 was obtained at 25°C which decreased gradually as the temperature was increased to 40°C when absorbance reached a value of 0.71. However, there was no significant change in absorbance value on increasing the temperature to 50°C. Thus, 40°C was considered to be the optimum temperature for laccase treatment. In the next step, neutral to acidic conditions (pH 3, 5 and 7) were used to study the effect of pH on the laccase treatment. The lowest value of absorbance was obtained at pH 5 (0.71) and so this value was considered as optimum. Finally, the concentration of laccase was optimized by performing experiments at concentrations of 500, 1000, 1500 and 2000 U l^{-1} laccase. Predictably, the absorbance value was highest (0.9) at the lowest concentration (500 U l^{-1}) and decreased at 1000 and 1500 U l^{-1} (0.71 and 0.68 respectively) of laccase. However, a further increase in concentration of laccase (2000 U l^{-1}) resulted in an increase in absorbance value (0.78). Thus a concentration of 1000 U l^{-1} laccase was taken as the optimum concentration for the treatment of samples dyed with dye **3** (3% o.m.f.) at pH 5 and 40°C for 2 hours in the presence of 1 mM l^{-1} HBT as mediator.

4.7.9 Assessment of Surface Dye Removal after Clearing with a Laccase from Trametes versicolor

The samples dyed with all the five dyes at a concentration of 3% o.m.f. were treated with laccase using the optimized conditions (Section 3.3.5). All the experiments were carried out in triplicate. Two control tests, one for HBT alone and the other for laccase in the presence of HBT, were also performed simultaneously. The absorbance values and concentration of the dyes in the acetone extract of the treated samples are given in Table 4.49. An interesting observation that is evident from the results in Table 4.49 is that the concentration of dye in the acetone extract is higher for the control containing HBT than the control without it. This suggests that a treatment of dyed fabric with buffer only under acidic conditions removes some of the surface dye. In fact, the amount of dye removed by buffer only is slightly greater than the amount of dye extracted with buffer in the presence of HBT.

Table 4.49 Amount of dye in the acetone extract of the dyed samples after treatment with laccase

Dye		Sample1		Sample2		Sample3		Average	
		λ_{max} (nm)	Absorbance	λ_{max} (nm)	Absorbance	λ_{max} (nm)	Absorbance	Absorbance	Conc. (mg l^{-1})
Dye **1**	Control	439	0.891	440	0.762	439	0.724	0.792	7.90
	Control (HBT)	440	0.896	440	0.885	439	0.844	0.875	8.73
	Laccase	439	0.655	439	0.626	439	0.713	0.665	6.63
Dye **2**	Control	511	1.2	511	1.156	511	1.011	1.122	13.54
	Control (HBT)	511	1.24	511	1.398	511	1.193	1.277	15.41
	Laccase	509	0.863	509	0.791	509	0.822	0.825	9.96
Dye **3**	Control	511	1.239	510	1.334	511	1.183	1.252	10.97
	Control (HBT)	511	1.329	511	1.343	511	1.318	1.330	11.65
	Laccase	506	0.671	507	0.675	506	0.772	0.706	6.19
Dye **4**	Control	630	0.312	630	0.317	630	0.271	0.300	3.85
	Control (HBT)	630	0.302	630	0.338	630	0.346	0.329	4.22
	Laccase	627	0.117	628	0.113	627	0.129	0.120	1.54
Dye **5**	Control	665	0.258	665	0.243	665	0.249	0.250	6.25
	Control (HBT)	665	0.287	664	0.27	665	0.238	0.265	6.63
	Laccase	666	0.195	665	0.207	666	0.176	0.193	4.82

The concentration of dye in acetone extract after treatment with laccase is significantly lower than the two controls indicating that enzyme treatment is able to remove surface dye. However, a comparison of the percentage of surface dye removed with reduction clearing using sodium dithionite shows that laccase removes significantly less dye than reduction clearing of the samples dyed with dyes **1**, **2** and **5** (Figure 4.72).

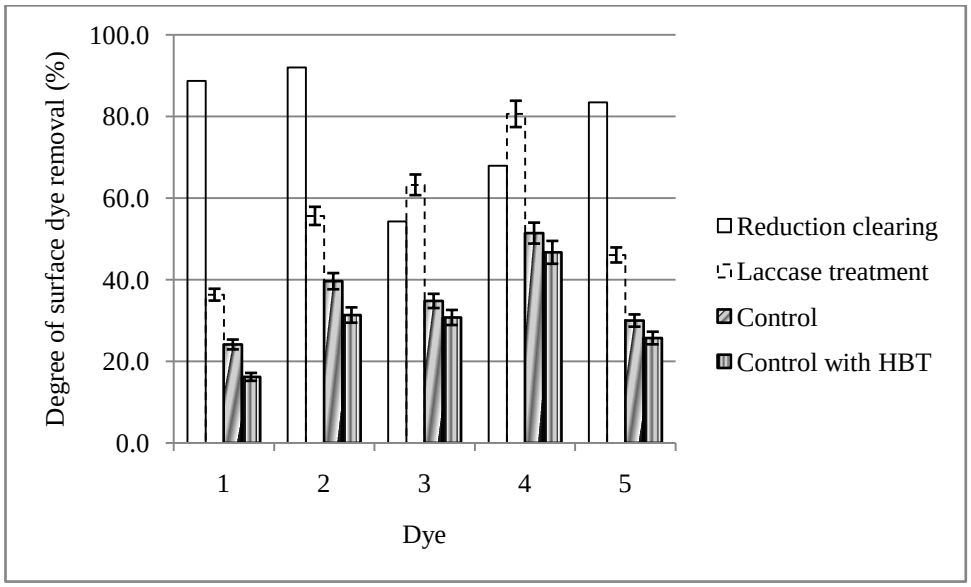


Figure 4.72 Degree of surface dye removal after treatment with a laccase from *Trametes versicolor*

Interestingly, the two dyes, **3** and **4**, which responded only moderately to reduction clearing (54% and 68% dye removal for dyes **3** and **4** respectively) gave a higher percentage of surface dye removal with the laccase treatment (63% and 80% respectively). This leads to a suggestion that dyes **3** and **4** may be more susceptible to oxidation than to reduction, at least under the conditions used. This appears more plausible for dye **4** as anthraquinone dyes have been reported to be resistant to reduction. It has been recommended to carry out oxidative clearing for the removal of surface deposits of anthraquinone dyes [9]. However, in the case of dye **3**, this behaviour is quite anomalous.

4.7.10 Washfastness Properties after Treatment with a Laccase from Trametes versicolor

The washfastness properties of samples dyed with all five dyes (3% o.m.f.) after treatment with laccase under the optimised conditions are given in Table 4.50. There are no significant changes in the washfastness properties of the samples after treatment with laccase which is correlated with the lower percentage of dye removal as determined by the acetone extraction of the treated samples. There is some

improvement in the washfastness of samples dyed with dye **4** which is in line with the concentration of dye **4** in the acetone extract. Dye **4** showed a slightly higher percentage of surface dye removal after treatment with laccase than reduction clearing but this difference has not translated into an improvement in the washfastness properties. This may be because of the rather small difference between the concentrations of dye in the acetone extracts after treatment of the dyed samples with the enzyme.

Table 4.50 Washfastness properties of the dyed samples after treatment with a laccase from *Trametes versicolor*

		Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
Dye **1**	Untreated	5	5	5	4	5	4
	Reduction Cleared	5	5	5	5	5	5
	Laccase	5	5	5	4-5	5	4
Dye **2**	Untreated	4	4-5	3	2-3	4-5	1-2
	Reduction Cleared	5	5	5	5	5	4-5
	Laccase	4-5	4-5	3-4	2-3	4-5	2
Dye **3**	Untreated	4	5	3-4	2-3	5	2-3
	Reduction Cleared	4	4-5	4	2-3	4-5	3
	Laccase	4-5	4-5	3-4	2-3	4-5	2-3
Dye **4**	Untreated	4	5	4	2-3	4-5	3-4
	Reduction Cleared	4-5	5	4-5	3-4	5	4-5
	Laccase	4-5	5	4-5	3-4	5	4-5
Dye **5**	Untreated	4-5	5	5	5	5	5
	Reduction Cleared	5	5	5	5	5	5
	Laccase	5	5	5	5	5	5

Thus, treatment with laccase does not provide improvement of the washfastness properties except for dye **4** in which case it gives similar results to that for reduction clearing with sodium dithionite. However, when compared with the treatment with cutinase NS29076, as described in Section 4.7.4, with reference to Table 4.45, there is no deterioration in the washfastness properties after laccase treatment.

4.7.11 Rubfastness Properties after Treatment with a Laccase from Trametes versicolor

Rubfastness properties of the dyed samples after treatment with a laccase from *Trametes versicolor* are given in Table 4.51. There is a slight improvement of the rating for dry rubfastness of all the dyed samples while there is no change in the wet rubfastness properties of any of the dyed samples after treatment with laccase. In contrast to the treatment with NS29076, laccase does not result in a deterioration in the fastness properties.

Table 4.51 Rubfastness properties of the dyed samples after treatment with a laccase from *Trametes versicolor*

		Dry	Wet
Dye **1**	Untreated	4-5	4-5
	Reduction Cleared	5	5
	Laccase	5	4-5
Dye **2**	Untreated	4	4
	Reduction Cleared	5	5
	Laccase	4-5	4
Dye **3**	Untreated	4	4-5
	Reduction Cleared	4-5	5
	Laccase	4-5	4-5
Dye **4**	Untreated	4-5	4
	Reduction Cleared	5	5
	Laccase	5	4-5
Dye **5**	Untreated	5	5
	Reduction Cleared	5	5
	Laccase	5	5

4.7.12 Colour Properties after Treatment with a Laccase from Trametes versicolor

The colour properties of the samples dyed with all the five dyes at 3% o.m.f. after treatment with laccase are given in Table 4.52.

Table 4.52 Colour measurements of the dyed samples after treatment with a laccase from *Trametes versicolor*

	Sample	L*	a*	b*	C*	h°	Integ value
Dye **1**	Untreated	77.71	16.91	99.83	101.25	80.38	26.29
	Laccase	77.82	17.49	100.97	102.47	80.17	27.79
Dye **2**	Untreated	24.48	33.62	7.22	34.39	12.12	47.8
	Laccase	24.16	33.88	7.07	34.61	11.78	49.4
Dye **3**	Untreated	23.56	31.81	8.05	32.81	14.2	51.48
	Laccase	23.53	32.47	7.89	33.41	13.66	52.0
Dye **4**	Untreated	22.18	6.21	-30.07	30.7	281.68	38.83
	Laccase	22.59	5.72	-30.32	30.85	280.68	38.09
Dye **5**	Untreated	40.6	-13.13	-34.14	36.58	248.97	15.8
	Laccase	40.5	-13.76	-32.93	35.69	247.32	15.76

The change in colour properties after treatment with both the enzymes and reduction clearing is given in Table 4.53 The change in lightness as indicated by the ΔL* values of the samples after treatment with the enzymes and sodium dithionite shows similar trend and the values are comparable. The only exception is observed in the case of samples dyed with dye **1**, in which case neither the values are comparable nor is there any specific trend. The same holds true for the differences in chroma of all the samples after treatment with enzymes as well as after reduction clearing, that is, only the samples dyed with dye **1** show a different response to laccase and NS29076. A similar trend is observed for the samples dyed with dyes **2-5** after treatment with laccase and with NS29076. The chroma of samples dyed with dyes **2**, **3** and **4** increases after treatment with laccase as it did after treatment with NS29076 and sodium dithionite. The change in chroma is greatest after reduction clearing in these three cases. In the case of samples dyed with dye **1** chroma increases after treatment with laccase and reduction clearing while it decreases after treatment with NS29076. The chroma of samples dyed with dye **5** decreases after treatment with the two enzymes, laccase and NS29076 while it increases after reduction clearing. Although, samples dyed with dye **4** give a higher percentage of dye removal (80%) after treatment with laccase compared to reduction clearing with sodium dithionite (68%), the laccase-treatment only produces

a very small change in chroma. The change in hue of the samples dyed with dyes **1**, **2** and **3** occurs in the same direction which is negative after the treatment with the two enzymes and reduction clearing.

Table 4.53 Differences in colour parameters after reduction clearing and treatment with NS29076 and a laccase from *Trametes versicolor*

Sample		ΔL*	Δa*	Δb*	ΔC*	ΔH*	ΔE (CMC)	Change in integ value
Dye **1**	Sodium dithionite	1.16	0.41	2.35	2.38	-0.01	0.81	0.76
	NS29076	-1.96	-0.11	-3.06	-3.03	-0.42	1.16	0.39
	Laccase	0.11	0.58	1.14	1.22	-0.38	0.42	1.5
Dye **2**	Sodium dithionite	-0.19	0.89	-0.38	0.8	-0.51	0.56	1.32
	NS29076	-0.49	0.12	-0.08	0.11	-0.1	0.36	2.35
	Laccase	-0.33	0.26	-0.16	0.22	-0.21	0.3	1.6
Dye **3**	Sodium dithionite	-0.14	0.78	-0.21	0.71	-0.4	0.46	2.75
	NS29076	-0.12	0.26	-0.05	0.24	-0.12	0.17	0.83
	Laccase	-0.03	0.66	-0.16	0.6	-0.31	0.37	0.52
Dye **4**	Sodium dithionite	0.26	0.15	-0.48	0.5	0.05	0.32	-0.65
	NS29076	0.3	-0.18	-0.23	0.19	-0.22	0.32	-0.73
	Laccase	0.41	-0.5	-0.25	0.15	-0.54	0.57	-0.74
Dye **5**	Sodium dithionite	0.06	1.01	-1.18	0.75	1.37	0.98	-0.02
	NS29076	0	0.24	0.33	-0.39	0.1	0.19	-0.33
	Laccase	-0.11	-0.64	1.21	-0.88	-1.04	0.81	-0.04

In the case of dye **4**, the hue of the dyed samples changes in the same direction after the two enzyme treatments whereas reduction clearing with sodium dithionite only produces a minor change. In the case of samples dyed with dye **5**, treatment with laccase produces a negative change while reduction clearing produces a positive shift. The colour differences after treatment with laccase are generally comparable to, but generally slightly less than those produced after reduction clearing. However, in the case of samples dyed with dye **4** colour differences (ΔE) are slightly greater after treatment with laccase than reduction clearing. Laccase treatment of samples dyed with dyes **1** and **2** produce a greater increase in the integ value than reduction clearing while in the case of dye **3**, this change is less than reduction clearing and for dyes **4** and **5** the change produced by both laccase and sodium dithionite is comparable. The integ values

of the two anthraquinone dyes **4** and **5** decrease after laccase treatment as well as reduction clearing and treatment with NS29076. In the case of dye **5** this change is rather insignificant after reduction clearing and treatment with laccase. Thus, it may be concluded that treatment with laccase produces effects on the colouristic properties of the dyed samples which are broadly similar to the changes produced by reduction clearing. The two enzymes also showed similar trends despite the fact that both operate by different mechanisms.

4.7.13 Scanning Electron Microscopy after Treatment with a Laccase from **Trametes versicolor**

The scanning electron micrographs of the all the dyed samples (3% o.m.f.) after treatment with laccase are given in Figure 4.73 - Figure 4.77. A number of images at various magnifications were taken, however, only a few selected images are presented here. These images show that the treatment with laccase results in a relatively cleaner fibre surface than the dyed samples. However, when compared with the SEM images after reduction clearing, a higher amount of superficial particles is observed after clearing with laccase.

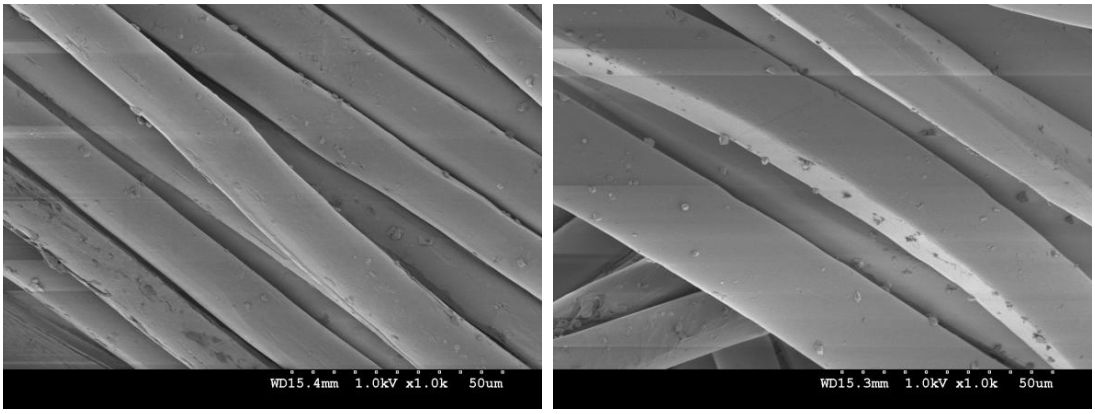


Figure 4.73 SEM images of samples dyed with dye **1** after treatment with laccase

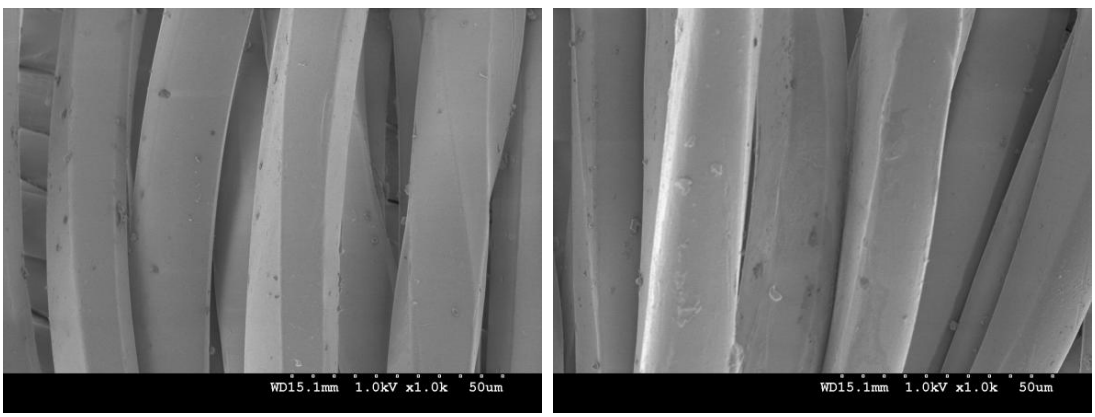


Figure 4.74 SEM images of samples dyed with dye **2** after treatment with laccase

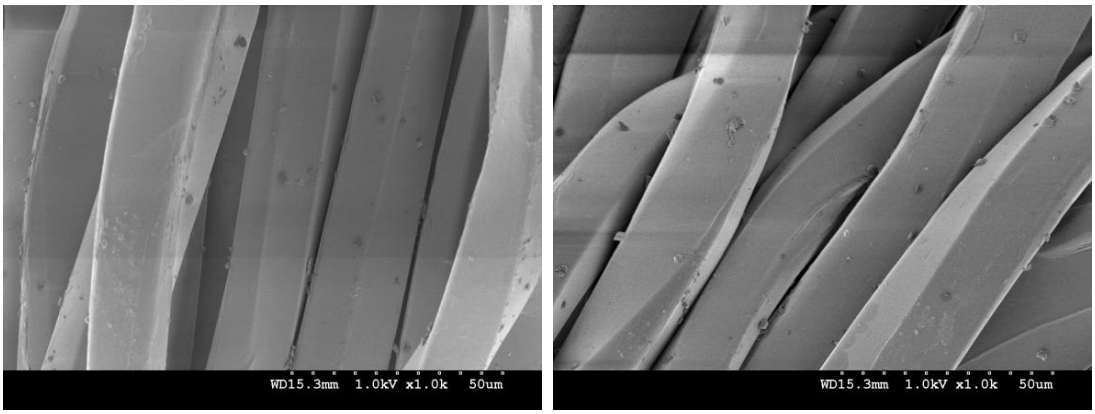


Figure 4.75 SEM images of samples dyed with dye **3** after treatment with laccase

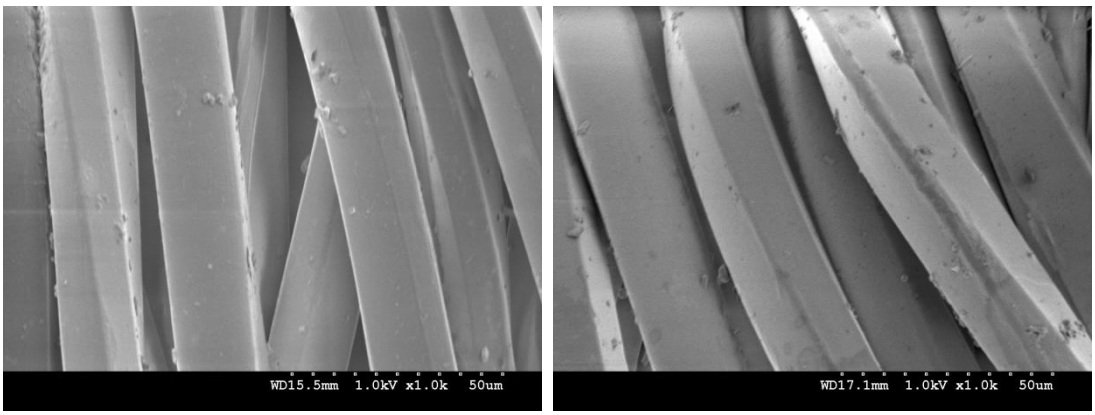


Figure 4.76 SEM images of samples dyed with dye **4** after treatment with laccase

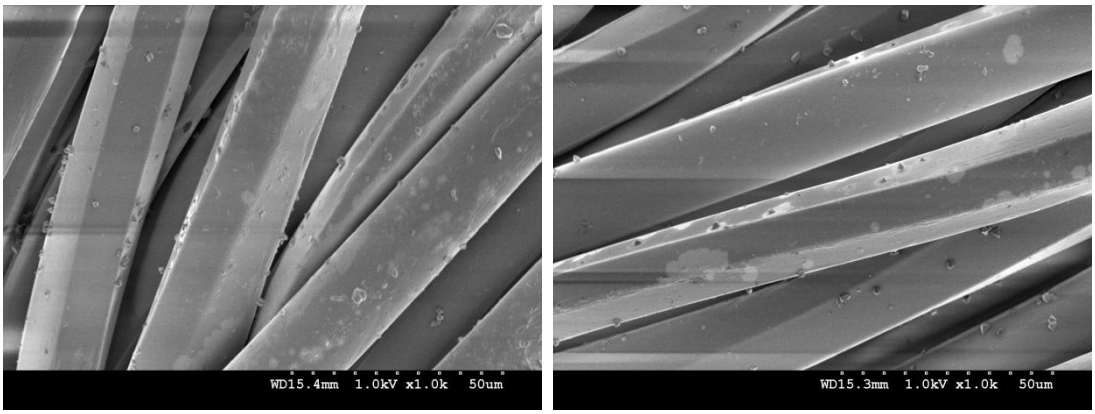


Figure 4.77 SEM images of samples dyed with dye **5** after treatment with laccase

4.8 Electrochemical Reduction Clearing

Reduction clearing involves the reduction of residual disperse dye present on the surface of dyed polyester. In the previous sections of this thesis, various reducing agents have been employed, both inorganic as well as organic, for this purpose. Electrochemical reduction methods have been utilized to reduce vat and sulphur dyes for textile applications in a number of studies as discussed in Section 2.7. In this section of the research, a preliminary attempt has been made to effect reduction clearing of disperse dyed polyester sample using electrochemical methods. For the reduction of vat and sulphur dyes, both direct and indirect methods of electrochemical reduction have been employed. In the case of reduction clearing of polyester, the indirect method appears to be more appropriate as the dye which is to be reduced is present on the fabric surface. An extensive literature review as presented in Section 2.7 led to the selection of three compounds which can be used as redox mediators for the reduction clearing of polyester. These compounds are iron-triethanolamine complex, iron-gluconate complex and anthraquinone-2-sulphonate. Iron salts have been used historically in textile dyeing applications, for example, the "copperas method" which involves the use of ferrous sulphate and calcium hydroxide for the reduction of vat dyes. A serious shortcoming of this process is the formation of bulky sediments which are produced because of the poor solubility of the ferrous hydroxide which is generated. Iron (II) gives a negative redox potential in alkaline solution at molar ratios of Fe(II):Fe(III) through 0.8:1 to 2:1. The disadvantages associated with this reducing agent include the instability of the iron salt complex in a weakly alkaline medium, the large quantity of iron salt required to provide a negative redox potential and a high content of metal ions [78]. The reaction of iron (II) salt with sodium hydroxide is given in Equation 4.4. It has been reported that precipitates of iron (II) hydroxide formed in the presence of sodium hydroxide can be complexed with aliphatic hydroxyl compounds containing a number of hydroxyl groups such as gluconic acid (Figure 4.78) or some amino compounds, for example triethanolamine (Figure 4.79), resulting in the development of the desired reduction potential in solution.

$$FeSO_4 + 2NaOH \rightarrow Fe(OH)_2 + Na_2SO_4 \qquad (4.4)$$

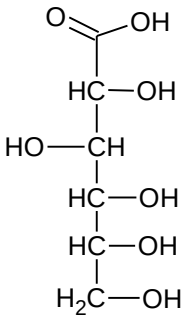


Figure 4.78 Chemical structure of gluconic acid

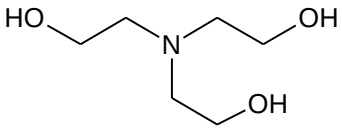


Figure 4.79 Chemical structure of triethanolamine (TEA)

Gluconic acid can be neutralized with alkali after the treatment while the iron (II) hydroxide may be converted to iron (III) hydroxide by aeration and then filtered/flocculated [14, 199]. Iron (II) chloride in the presence of twice the amount of gluconic acid as a complexing agent has been used for the reduction clearing of polyester in a previous study regarding the comparison of various reducing agents [11]. The iron-complex was shown to have a redox potential of -800 mV which is quite independent of the temperature and does not show any significant change above 40°C. It was reported that it consumed less oxygen than sodium dithionite. However, only 85% of the theoretically calculated value of iron-TEA complex reacts with oxygen. The iron-complex offers the advantage of a sulphur-free effluent but, on the other hand, the presence of gluconic acid increases the COD of the resulting effluent [11]. Quinones are considered to be active redox species in the reductive transformations of natural organic matter. Anthraquinone derivatives (such as alizarin) have also been used in traditional fermentation baths for indigo dyeing [126]. Selected derivatives of anthraquinone such as anthraquinone sulphonic acids and hydroxyanthraquinones have been reported as redox mediators for indirect electrochemical reduction of vat dyes [83]. Redox potential values of various quinone compounds have been compiled in a study [210]. It has been reported that anthraquinone-2-sulphonate does not undergo any decomposition over the whole pH range (0 – 14) [211].

Initially a set of experiments was carried out with the iron salt complexed with sodium gluconate as a reducing agent to establish whether it is able to reduce the dye without the use of electrochemical set-up. Before carrying out the electrochemical batch

experiments for reduction clearing of polyester fabric, the selected compounds were subjected to cyclic voltammetry experiments. The resulting data were used to calculate the redox potential values of the compounds which assisted in the selection of voltage and current for the subsequent reduction clearing experiments. The samples were rinsed as described for the previous experiments after reduction clearing and the efficiency of the treatment was assessed by measuring the absorbance of the acetone extract of the treated samples and washfastness.

4.8.1 Reduction Clearing with Iron Salts

An investigation was carried out into reduction clearing with iron (II) sulphate used with sodium D-gluconate (DGL) as a complexing agent in alkaline medium at the concentrations shown in Table 4.54. Initially the fabric samples dyed with dye **3** at 3% o.m.f. were treated with these solutions in the Pyrotec dyeing machine at 25°C for 20 minutes. The absorbance values of the acetone extract of these samples did not show significant dye removal as indicated by high values of absorbance (Table 4.54).

Table 4.54 Range of experiments for the treatment of samples dyed with dye **3** (3% o.m.f.) with iron (II) salt at 25°C and the respective absorbance values

Concentration of $FeSO_4.7H_2O$ (mM)	10	10	10	10	10	10
Concentration of NaOH (mM)	0	0	10	20	20	20
Concentration of DGL (mM)	0	10	10	0	10	20
Absorbance	1.10	1.07	1.0	0.90	1.06	0.95

The values obtained using varying concentrations of the three compounds, iron (II) sulphate, sodium hydroxide and sodium D-gluconate (DGL) were not significantly different from each other. The lowest value of absorbance (0.9) was obtained with iron (II) sulphate and alkali only. However, treatment with iron (II) sulphate alone resulted in an absorbance value of 1.096. The absorbance value of the acetone extract of the untreated samples dyed with dye **3** at 3% o.m.f. was 1.92 (Table 4.2). This implies that treatment with iron (II) sulphate does remove about 43% surface dye at 25°C. However, at this temperature, no differentiation can be made on the basis of these absorbance values, among various combinations of iron salt, complexing agent (DGL) and alkali at different concentrations. Hence, selected experiments were repeated at a higher temperature of 60°C (Table 4.55).

Table 4.55 Range of experiments for the treatment of samples dyed with dye **3** (3% o.m.f.) with iron (II) salt at 60°C and the respective absorbance values

Concentration of $FeSO_4.7H_2O$ (mM)	0	10	0	10	0
Concentration of NaOH (mM)	0	0	0	0	20
Concentration of DGL (mM)	0	0	20	20	10
Absorbance	1.92	1.19	0.94	1.06	0.72

At 60°C, the lowest value of absorbance (0.72) is obtained with a combination of DGL and alkali only. This indicates that sodium gluconate is able to remove surface dye presumably acting as a reducing agent under alkaline conditions. In fact, a comparison with the absorbance values given by extracts of samples reduction cleared with sodium dithionite (0.878, Table 4.2) shows that sodium gluconate may be as suitable a reducing agent as sodium dithionite at least in the case of dye **3**.

4.8.2 Cyclic Voltammetry Experiments

The three redox mediators, iron-triethanolamine (TEA) complex, iron-sodium gluconate (DGL) complex and 9,10-anthraquinone-2-sulphonate (AQS) selected for electrochemical reduction clearing were characterized by cyclic voltammetry under alkaline conditions initially and afterwards with the addition of a 0.1 g l^{-1} dispersion of dye **3** to investigate the behaviour of the redox mediators in the presence of a reducible species. The composition of the solutions used (1-3) is given in Table 4.56. Cyclic voltammetry of a dispersion of dye **3** in phosphate buffer was also carried out for comparison purposes.

Table 4.56 Concentrations of mediator solutions used for cyclic voltammetry

Solution	$FeCl_3$	Triethanolamine (TEA)	Sodium D-gluconate (DGL)	9,10-anthraquinone-2-sulphonate (AQS)	KOH
1	0.0078 M	0.038 M	-	-	0.15 M
2	0.01 M	-	0.02 M	-	0.2 M
3	-	-	-	1 mM	0.1 M

(a) Iron-TEA Complex

A cyclic voltammogram (CV) can be used to provide important qualitative and quantitative information about the reaction under study. The first important information concerns the reversibility of the reaction. For a reversible process, the ratio of the anodic peak current (Ip,a) to the cathodic peak current (Ip,c) is unity. If the value deviates from 1, this indicates kinetic or other complications in the electrode process. If

there is further reaction at the electrode after the initial electron transfer, for example in the presence of dye, which destroys the product formed at the cathode before the reverse scan, then the ratio of the cathodic peak current to anodic peak current becomes greater than 1. The values of cathodic and anodic peak currents are read directly from the CV (Figures 4.69 – 4.72) and are given in Table 4.57 for solution 1 (iron-TEA). This ratio (Ip,a/Ip,c) is close to 1 for the iron-TEA complex at all scan rates indicating that the reaction is reversible. The difference between the anodic peak potential (Ep,a) and cathodic peak potential (Ep,c) should be about 0.06 V (60 mV) for a one electron transfer [212, 213]. In the case of the iron-TEA complex, this difference is about 0.09 V at a scan rate of 0.01 V s^{-1} and gradually increases with increasing scan rate. This may be explained on the basis of the type of electrode used. Peak separations of 0.06 V are generally obtained on electrode surfaces which are highly catalytic for that process, for example the mercury drop electrode. In this study, a glassy carbon electrode was used and it is known that there is a tendency for absorption on the electrode surface which gives higher values. The values of cathodic peak potential (Ep,c) and anodic peak potential (Ep,a) are also obtained from the voltammogram (Figure 4.80). For an ideally reversible system, the peak potential should not change with the scan rate. The peak potentials of the iron-TEA complex change slightly with the scan rate, thus indicating that this system is not ideally reversible. The values of cathodic and anodic peak potentials obtained at a scan rate of 0.05 V s^{-1} have been used to calculate the reduction potential which is -1.05 V as shown in Table 4.57.

Table 4.57 Peak currents and potentials of solution 1 (iron-TEA complex) as obtained from CV

	Ep,a (V)	Ep,c (V)	Ip,a (μA)	Ip,c (μA)	ν (V s^{-1})	E_{mid} ($E_{1/2}$) (V)	Ip,a/Ip,c	$\nu^{1/2}$	e.f.	Ep,a-Ep,c (V)
Iron-TEA	-0.99	-1.08	127.4	110	0.01	-1.03	1.16	3.16	1.3	0.09
	-0.97	-1.10	202	182	0.02	-1.03	1.11	4.47	1.0	0.13
	-0.95	-1.13	309	267	0.04	-1.04	1.16	6.32	1.0	0.18
	-0.93	-1.19	198	232	0.05	-1.06	0.85	7.07	1.3	0.26
	-0.94	-1.15	451	361	0.08	-1.04	1.25	8.94	0.9	0.22
	-0.93	-1.14	349	375	0.1	-1.03	0.93	10.0	1.1	0.21
	-0.92	-1.17	536	410	0.12	-1.04	1.31	10.95	1.0	0.25
	-0.91	-1.19	573	450	0.15	-1.05	1.27	12.25		0.28
	-0.83	-1.29	365	423	0.2	-1.06	0.86	14.14	1	0.46
Iron-TEA + Dye **3**	-0.97	-1.10	142	142	0.01	-1.03	1.00	3.16		0.13
	-0.96	-1.11	217	191	0.02	-1.04	1.14	4.47		0.15
	-0.94	-1.13	309	266	0.04	-1.04	1.16	6.32		0.19
	-0.96	-1.14	365	309	0.05	-1.05	1.18	7.07		0.18
	-0.93	-1.15	360	323	0.06	-1.04	1.11	7.75		0.22
	-0.93	-1.15	393	330	0.08	-1.04	1.19	8.94		0.22
	-0.91	-1.17	532	399	0.1	-1.04	1.33	10.00		0.27
	-0.90	-1.19	456	393	0.12	-1.05	1.16	10.95		0.29
	-0.75	-1.17	696	508	0.2	-0.96	1.37	14.14		0.42

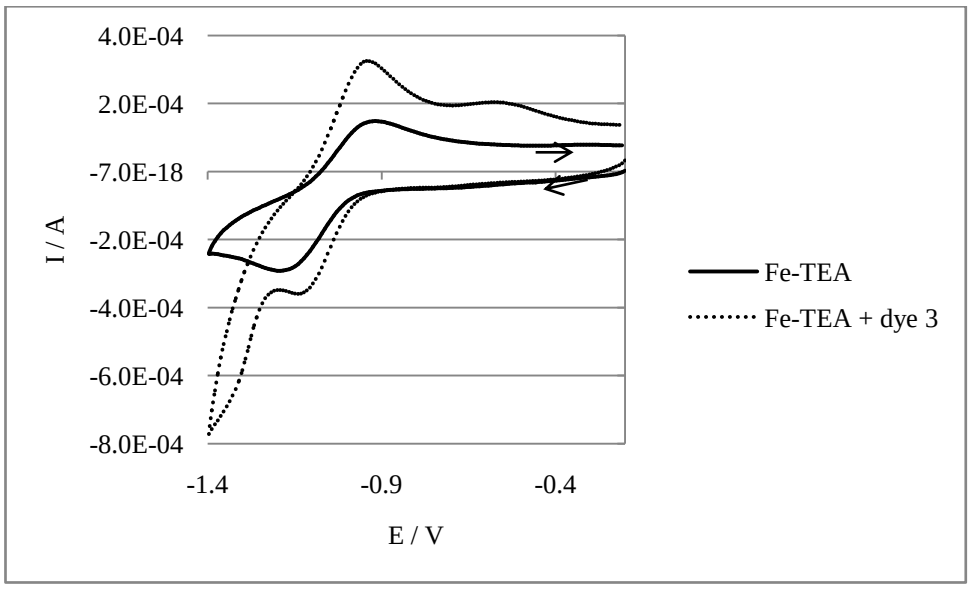


Figure 4.80 CV of solution 1 (iron-TEA) before and after the addition of dye **3** at a scan rate of 0.05 V s^{-1}

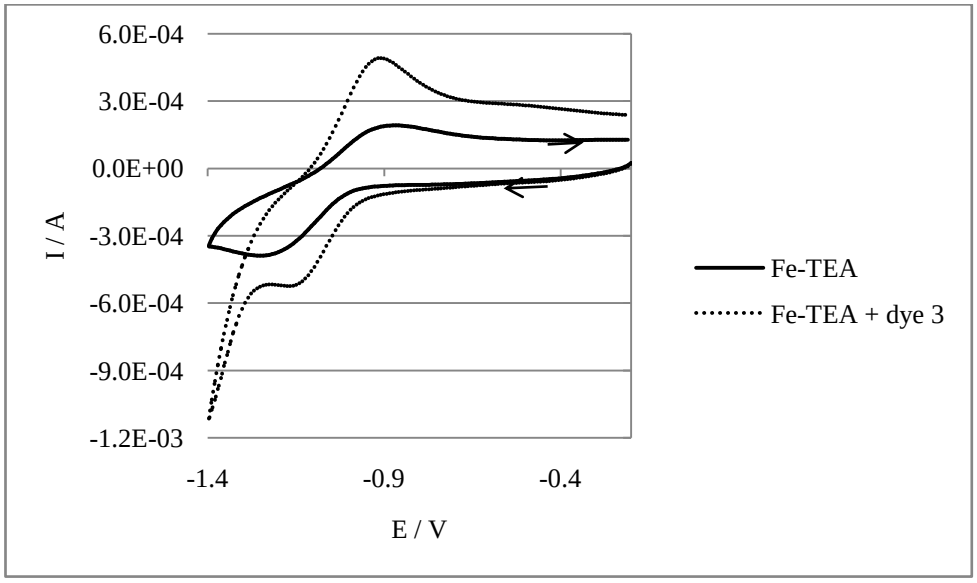


Figure 4.81 CV of solution 1 (iron-TEA) before and after the addition of dye **3** at a scan rate of 0.1 V s^{-1}

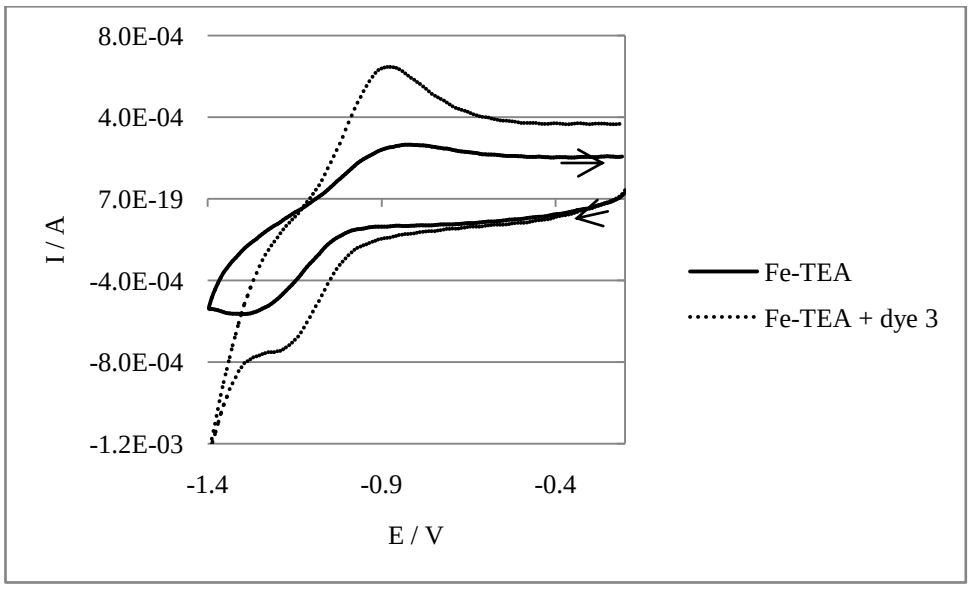


Figure 4.82 CV of solution 1 (iron-TEA) before and after the addition of dye **3** at a scan rate of 0.2 V s^{-1}

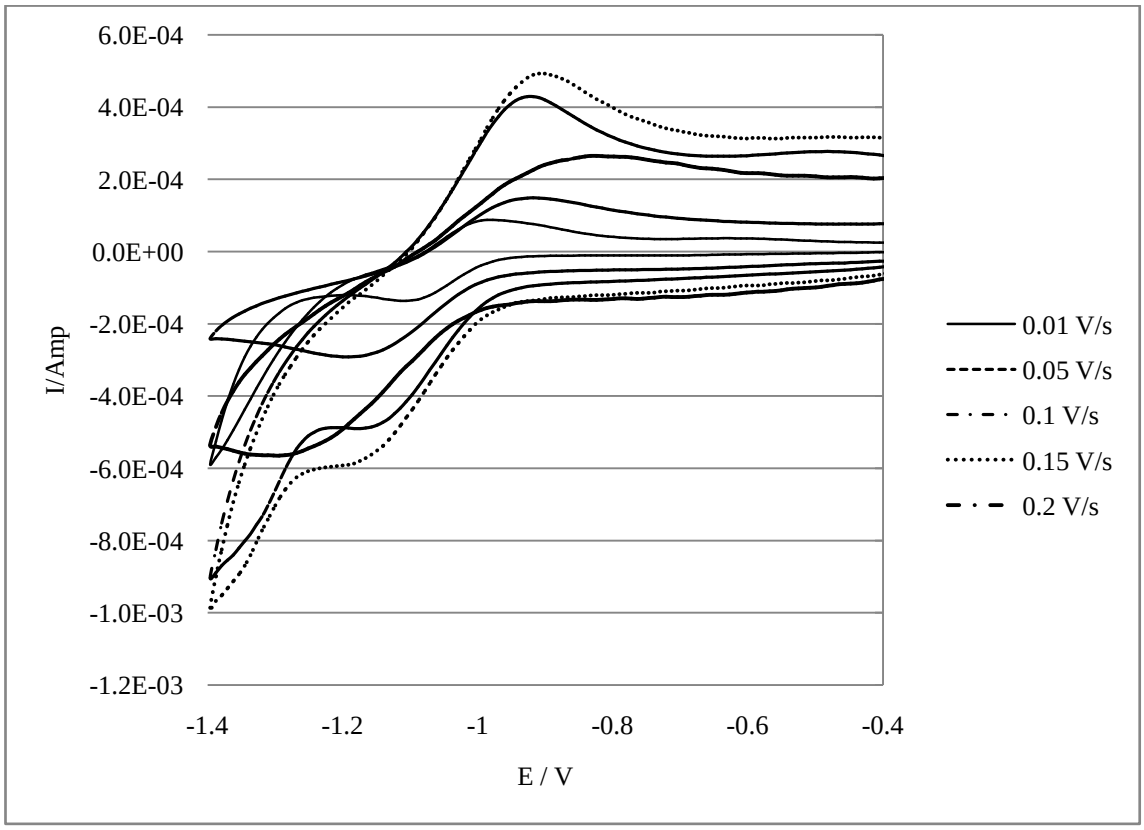


Figure 4.83 Scan rate dependence of solution 1 (iron-TEA)

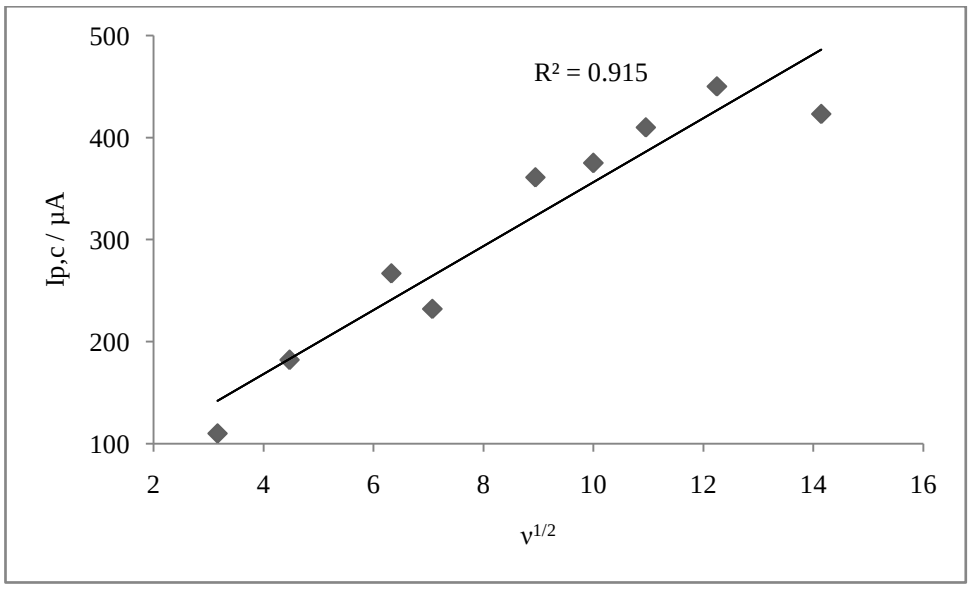


Figure 4.84 Relation between cathodic peak current and scan rate for solution 1 (iron-TEA)

The peak current (Ip,c) is linearly proportional to the square root of scan rate ($\nu^{1/2}$) for a diffusion controlled, reversible system. The iron-TEA system fits this proportionality reasonably as shown in Figure 4.84. Such dependence shows that reaction is diffusion controlled.

The CV for dye **3** in phosphate buffer is illustrated in Figure 4.85. This voltammogram shows that there is no redox activity within the potential range studied under the conditions used.

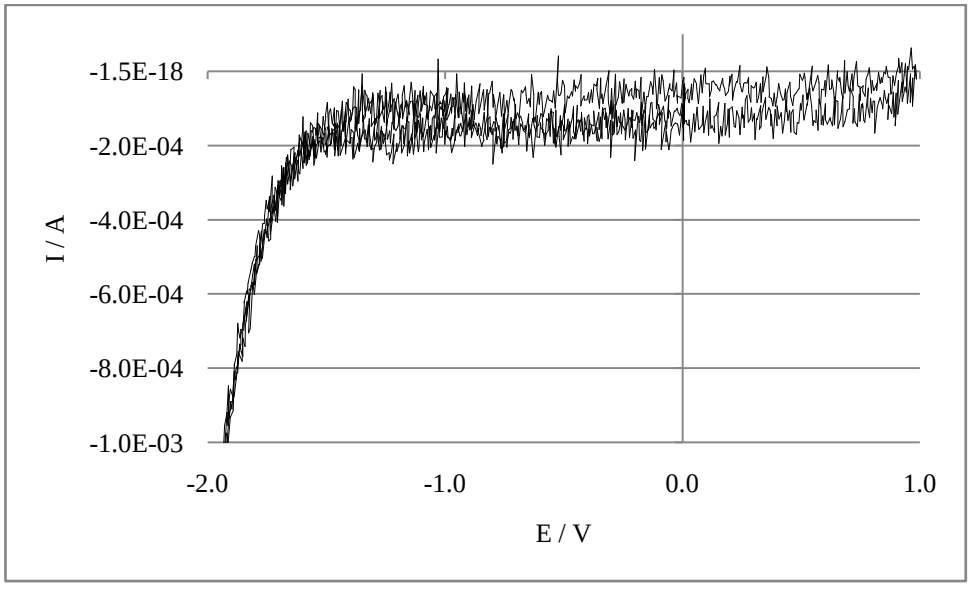


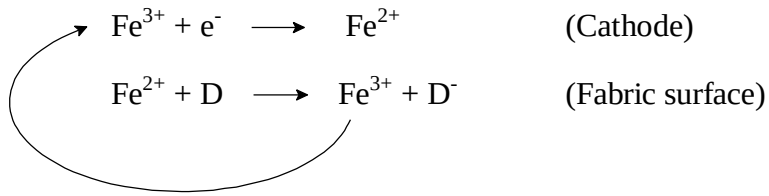
Figure 4.85 Cyclic voltammogram for dye **3** (100 mg l^{-1}) in 0.066 M Na_2HPO_4

The CV for the iron-TEA complex shows an increase in cathodic and anodic currents after the addition of dye **3** (Figures 4.69 – 4.71). As the current is directly proportional

to the concentration of the electroactive species, which in this case is iron(III)-TEA/iron(II)-TEA, this indicates that an increased amount of iron (III) is present at the electrode surface generated by the indirect reduction of the dye after the addition of dye. Also, the anodic peak reflects the amount of iron (II) present at the electrode surface, and this increases as it is being generated by the reduction of the iron (III) on the cathodic sweep. The increase in the height of the anodic peak is greater than the increase in the height of cathodic peak after the addition of dye. Since there is only a very small amount of dye in the bath, all the iron (II) generated at the electrode is not being consumed by the dye molecules. The other two interesting features which appear after the addition of dye are observed at -1.35 V in the forward scan and at about -0.5 V during the reverse scan after the major anodic peak (Figure 4.80). It has been reported in the literature that iron (II) can reduce azo dyes to aryl amines [85, 140]. Thus, the secondary anodic peak in the reverse scan may be due to the interaction of the dye with the electrode directly, involving either direct reduction of dye or due to auxiliaries or impurities in the dye sample. This wave feature during the anodic (reverse) scan at -0.5 V in the reverse scan disappears with the increase in scan rate (Figure 4.81 & Figure 4.82). The anodic peak potential remains unchanged after the addition of dye but there is a slight shift towards positive potential in the cathodic peak after the addition of dye. The second cathodic peak at -1.4 V in the forward scan at the switching potential becomes sharper while the first cathodic peak becomes broader with increasing scan rate. A sharp peak (smaller difference between cathodic half peak potential and cathodic peak potential) signifies fast electron transfer kinetics.

The enhancement factor (e.f.) may be used as an indicator of the efficiency of a redox system in terms of its ability to reduce a particular species. This factor is the ratio of the cathodic peak current of the redox system, referred to as diffusion current, to the cathodic peak current after the addition of the dye, referred to as catalytic peak current. The enhancement factor for the iron-TEA complex is greater than 1 which indicates the suitability of this system for the reduction of dye **3**. However, the e.f. values obtained in this experiment are lower than those quoted in the literature for iron-amino complexes, which is around 4 [214]. Enhancement factor depends upon the scan rate and the concentration of the dye dispersed in the solution. Generally, the factor increases with the concentration of the dye up to a maximum and then drops. At the same time, there is an inverse relationship with the scan rate, e.f. values decreasing at higher scan rates [215]. However, no significant difference in the e.f. values determined

at low and high scan rates was observed in this study. The indirect electrochemical reduction of dye **3** can be categorized as an ECE reaction represented by Scheme 4.1, as discussed in Section 0.



Scheme 4.1 Indirect electrochemical reduction of dye using iron salt as redox mediator

Probably within the limits of experimental error, the ratio of peak currents is quite close to unity with and without dye. This indicates that the products formed by reduction are chemically stable [216]. The enhancement in the cathodic current in the presence of the dye is consistent with the processes as illustrated in Scheme 4.1 as more Fe (III) becomes available at the electrode surface from reduction of the dye.

(b) 9,10-Anthraquinone-2-sulphonate Sodium Salt

The CVs for the solution 2 (AQS), with and without the addition of dye **3** at ambient temperature and heated to around 40°C are shown in Figure 4.86 - Figure 4.88.

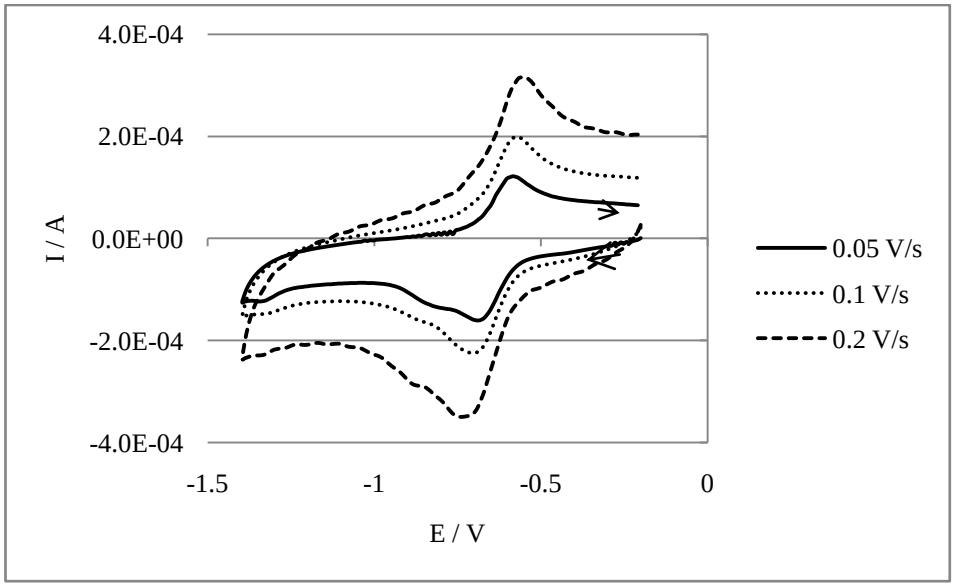


Figure 4.86 CV of solution 2 (AQS) at various scan rates showing the scan rate dependence

Three peaks are observed in the cathodic forward scan at -0.67 V, -0.8 V and -1.3 V for the solution 2 (AQS only) (Figure 4.86). Small shoulders are also observed in the CV of the anthraquinone at the base of the cathodic and anodic peaks. According to

previous studies, this feature may be due to some irreversible redox reactions or due to the presence of complexes of different stabilities in the solution [212].

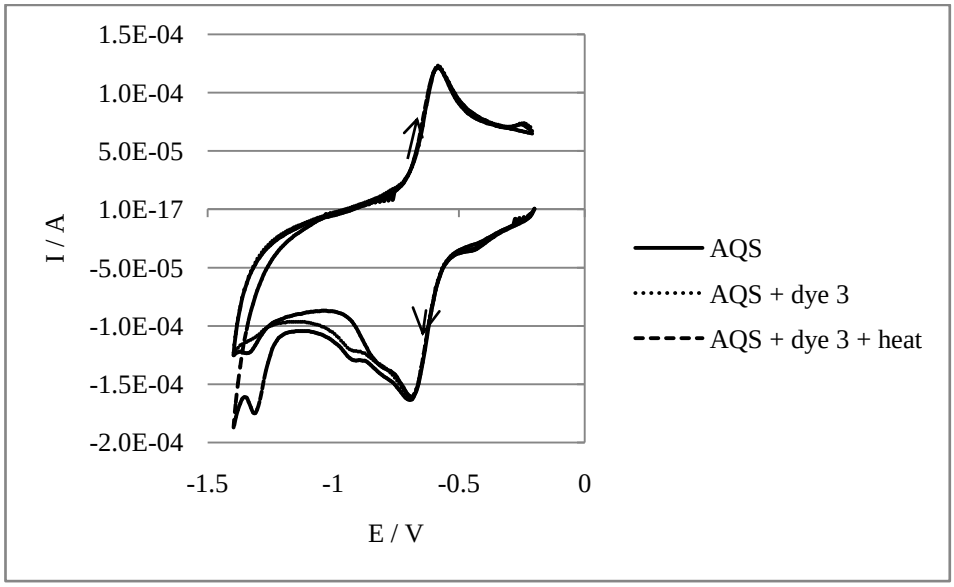


Figure 4.87 CV of solution 2 (AQS) with and without the addition of dye **3** and after heating at a scan rate of 0.05 V s^{-1}

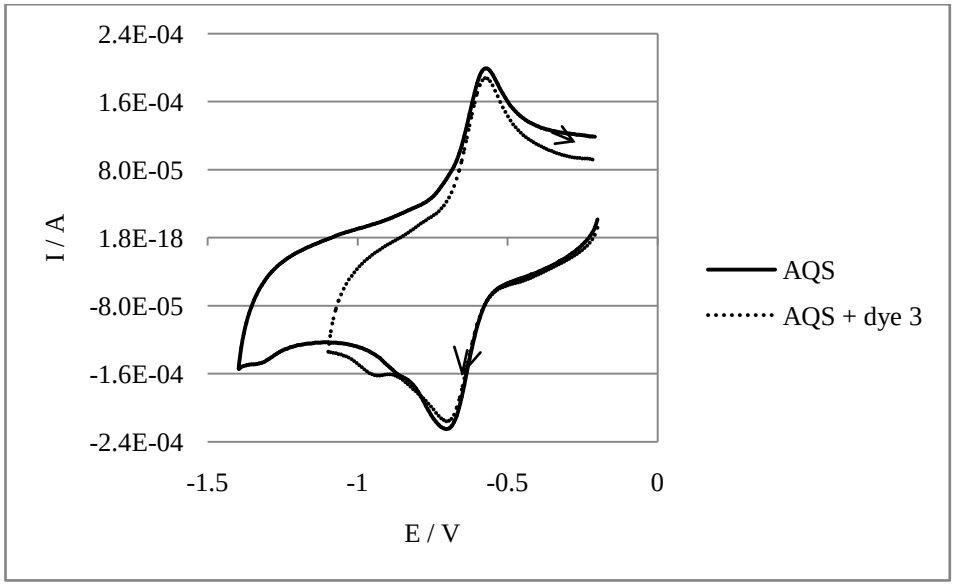


Figure 4.88 CV of solution 2 (AQS) with and without the addition of dye **3** at a scan rate of 0.1 V s^{-1}

Unlike the CV of the iron-TEA complex, no catalytic current is observed in the CV of the anthraquinone since there is no increase in peak height as shown in Figure 4.87 & Figure 4.88. This indicates that the addition of the dye does not affect the electrochemical behaviour of the anthraquinone and there is no reduction of dye by the

anthraquinone. Another possibility may be that the rate of reduction of dye is quite slow relative to the time scale of CV experiments and no change is detected at a high scan rate and low dye concentration. As illustrated in Figure 4.87, a distinct feature is found at −0.95 V in the cathodic scan after the addition of dye which is relatively unaffected at the higher temperature. However, the peak at −1.3 V is enhanced on heating. This peak is observed just before the switching potential and becomes especially pronounced by the application of heat to the anthraquinone and dye solution. The cathodic peak potential is −0.69 V at a scan rate of 0.050 V s^{-1} which is also close to the value previously described in literature, which was −0.62 V vs. Ag/AgCl/3M KCl at a scan rate of 0.01 V s^{-1} and −0.75 V at a scan rate of 0.05 V s^{-1}[14, 132, 217].

Table 4.58 Values of peak potentials and peak currents of solution 2 (AQS) as obtained from the CV

	Ep,a	Ep,c	Ip,a	Ip,c	ν	E_{mid} ($E_{1/2}$)	Ip,a/Ip,c	$\nu^{1/2}$	e.f.	Ep,a-Ep,c
	V	V	µA	µA	V s^{-1}	V				V
AQS	-0.59	-0.69	117	114	0.05	-0.64	1.03	7.07	0.9	0.094
	-0.58	-0.69	136	152	0.1	-0.64	0.89	10	0.91	0.103
	-0.57	-0.70	203	194	0.2	-0.64	1.05	14.1		0.137
AQS + dye **3**	-0.60	-0.67	41.7	43.6	0.01	-0.64	0.96	3.16		
	-0.60	-0.67	55.5	62.4	0.02	-0.64	0.89	4.47		
	-0.60	-0.67	76.8	86	0.04	-0.64	0.89	6.32		
	-0.59	-0.68	114	103	0.05	-0.64	1.11	7.07		
	-0.60	-0.68	89	111	0.06	-0.64	0.80	7.75		
	-0.59	-0.68	79	86	0.08	-0.64	0.92	8.94		
	-0.59	-0.68	119	138	10.	-0.64	0.86	10		
	-0.58	-0.70	136	140	0.12	-0.64	0.97	11		
AQS + dye **3** (after heating)	-0.58	-0.69	124	147	0.05	-0.64	0.84	7.07	1.29	

The data obtained from the CV of 9,10-anthraquinone-2-sulphonate are tabulated in the Table 4.58. The reduction potential of 9,10-anthraquinone-2-sulphonate has been calculated as -0.64 V using a scan rate of 0.05 V s^{-1}. The enhancement factor is 0.9 at a scan rate of 0.050 V s^{-1} which increases to 1.29 after heating the solution. This value is in reasonable agreement with the value cited in literature for the reduction of an azo dye by 9,10-anthraquinone-2-sulphonate (1.17 vs Ag/AgCl 3M NaCl) [218]. It has also

been suggested that the e.f. values decrease at high scan rates of 0.050 – 0.1 V s^{-1} due to the slow rate of reaction between dye and mediator [214].

(c) Iron-gluconate Complex

The CV of the iron-gluconate complex is shown in Figure 4.89. This graph does not indicate reversibility of the redox system and thus the CV does not provide information such as peak potentials as were obtained in the case of the iron-TEA complex and AQS.

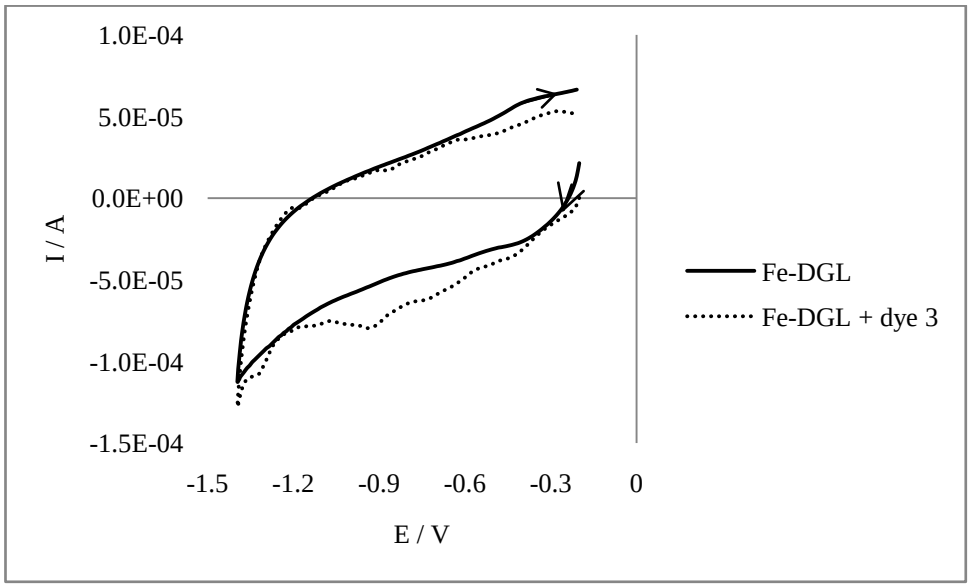


Figure 4.89 CV of solution 3 (iron-gluconate) with and without the addition of dye **3** at a scan rate of 0.050 V s^{-1}

Nevertheless, the CV does show some changes after the addition of dye. There is an evolution of a cathodic peak at -0.9 V with the dye present but no peak on the reverse sweep. In a previous study, an iron (III)-oxalate-gluconate complex has been suggested as a redox mediator in place of iron-amine complexes as a cheaper and greener alternative [15]. The iron (III)-gluconate system is reported to be comparatively difficult to reduce electrochemically. However, there is a possibility that a small amount of iron (III)-gluconate may be reduced in the process. The e.f. for iron (III)-DGL complex has been quoted as 1.8 in the presence of 0.5 g l^{-1} vat dye at scan rates of 0.05-0.1 V s^{-1} while the dye concentration is about five times less than that in the experiments described in this thesis [14]. This may be a reason for a CV without any reduction/oxidation peaks and thus the inability to determine the redox potential from CV.

4.8.3 Batch Electrolysis Experiments

Batch electrolysis experiments to investigate electrochemical reduction clearing of samples dyed with disperse dye **3** were carried out for 20 minutes at controlled potential values of −1.1 V for solution 1 and at −0.7 V for solutions 2 and 3 respectively using the three mediators as defined in Table 4.56. This followed the general recommendation to carry out the experiments at about 200 mV more negative compared with the redox potential determined. However, this may not be possible for all the cases due to the electrolysis of the other electroactive species present in the solution. These experiments require a different type of cell construction other than that used for cyclic voltammetry experiments. For example, the area of the working and counter electrodes should be large enough. There should be sufficient stirring of the solution to ensure uniform distribution of the electroactive species and to increase the rate of mass transport of the redox species from and towards the electrode. Also, the auxiliary electrode is required to be separated from the working electrode to avoid the interference caused by the species generated at the counter electrode. The material used for the isolation of the two electrodes should not have a high resistance; otherwise the efficiency of the electrolysis is reduced. Solution 1 and solution 3 were also used for batch experiments for longer time periods that is 90 min and 60 minutes respectively. All the experiments were carried out with continuous bubbling of nitrogen to reduce any interference that can be caused by atmospheric oxygen.

The fabric samples were tested after batch electrolysis to assess the extent of reduction clearing by measuring the absorbance of the acetone extract and also washfastness of the treated samples. The results of both the tests and a comparison with conventional reduction clearing with sodium dithionite (from Table 4.2 & Table 4.5) are given in Table 4.59. The results of the absorbance of the acetone extract show that there is some dye removal after electrochemical reduction clearing. The washfastness rating as judged by nylon staining is only 2-3, which is, however, poorer than the results obtained after conventional reduction clearing. These results thus indicate that the reduction clearing by the electrochemical method does not improve the washfastness properties of the samples dyed with dye **3**. It is also observed that the washfastness results of samples dyed with dye **3** after electrochemical reduction clearing with the three mediator systems are similar. This is not consistent with the redox potential of these solutions as determined from their respective CVs. The redox potential of solution 1 is -1.05 V while that of solution 3 is -0.65 V, almost half the value. Even with such a

large difference in the redox potentials of these solutions, the fastness properties are similar. Thus the difference in redox potentials does not appear to have a significant influence on the fastness properties.

Table 4.59 Assessment of the efficiency of the electrochemical reduction clearing (at controlled potential) of samples dyed with dye **3**

Solution	1	2	3	Sodium dithionite	1	3	4	5
Time (min)	20	20	20	20	90	60	40	30
Absorbance of the acetone extract	0.81	1.12	1.09	0.88	0.88	0.90	0.89	0.10
Wash fastness - Staining								
Wool	4-5	4-5	4-5	4-5	4	4	4	4
Acrylic	5	5	5	5	4-5	4-5	4-5	4-5
Polyester	4	4	4	4	4	4	4	3-4
Nylon	3	2-3	3	3-4	2-3	2-3	2-3	2-3
Cotton	5	5	5	5	5	5	5	4-5
Acetate	2-3	2-3	2-3	3-4	2-3	2-3	2-3	2-3

The redox potential of sodium dithionite during a conventional reduction clearing process is about -0.935 V. The washfastness properties after electrochemical reduction clearing with solution 1 as mediator do not improve when the time of the process is increased to 90 minutes. In fact the washfastness ratings after conventional reduction clearing which was carried out for only 20 minutes are better than the electrochemical reduction clearing which was carried out for 90 minutes with a redox mediator whose reduction potential is higher than sodium dithionite. To investigate the effect of pH on electrochemical reduction clearing, solution 4 was used for electrochemical reduction clearing at a potential of -1.2 V for 40 minutes. However, the fastness results again failed to show any differences. These results indicate that the rate of electrochemical reduction clearing may be too slow. To increase the rate, three different approaches may be employed, which are, to increase the concentration of the reducing species, to increase the surface area of the cathode or to increase the applied current. Thus, in the next step of this study (solution 5, Table 3.4), higher concentrations of the iron (III) chloride were used. However, this had no influence on the washfastness results and the washfastness properties did not improve.

Since the experiments performed using controlled potentials did not demonstrate differences among the three mediators, further experiments were carried out under

controlled current conditions for solution 1 only. The current was set at 0.25 A and 0.5 A for 40 minutes and 20 minutes respectively with the fabric samples (samples named A and B respectively). The results of the absorbance values given by the acetone extract of the treated samples and their washfastness is given in Table 4.60. The absorbance values of the acetone extract of the sample B is lower than sample A, which may indicate that a higher current is more effective in the removal of surface dye. However, the washfastness ratings of both the samples are similar.

Table 4.60 Assessment of the efficiency of the electrochemical reduction clearing (at controlled current) of samples dyed with dye **3** using solution 1 as redox mediator

Sample	A	B	C
Absorbance	0.95	0.88	0.89
Washfastness-Staining			
Wool	4	4	4
Acrylic	4-5	4-5	4-5
Polyester	4	4	4
Nylon	2-3	2-3	2-3
Cotton	5	5	5
Acetate	3	3	3

In the next experiment, the current was set at 0.25 A for 1.5 hours at which point the evolution of hydrogen was observed. The redox potential was measured with a KCl electrode and was found to be –1.06 V when hydrogen evolution started. The electrochemical cell was then switched off, electrodes taken out and dyed fabric was placed in the catholyte. This sample, named sample C, was kept in the catholyte for 3 hours. Redox potential was monitored regularly during this time and it was found that it had reduced to –0.953 V after 3 hours when the sample C was taken out. However, the extract-absorbance value and washfastness properties of sample C were similar to samples A and B.

A feature that should be noted is that during the electrochemical reduction the redox potential of the species is determined at the surface of electrode which may be different from the redox potential in the bulk. However, during conventional reduction clearing, the reducing agent generates the reduction potential in the bulk solution. A significant improvement in washfastness can be observed at lower reduction potentials of –600 to –700 mV for example, when reduction clearing with glucose and hydroxyacetone. It

can thus be inferred that to achieve effective electrochemical reduction clearing, conditions in which a reduction potential which is distributed throughout the solution rather than localised at the electrode surface have to be considered.

4.9 Redox Potential of the Clearing Agents

The redox potential of the various clearing agents, which comprised reductive as well as oxidative agents, was measured under the test conditions used for the clearing of dyed samples to investigate the relationship between clearing efficiency and redox potential. The values were measured with a redox meter as described in Section 3.3.10 and are given in Table 4.61. All the compounds were used at the concentration and under conditions which were utilized for the clearing of the dyed samples. However, the redox potential of glucose was measured at a lower temperature of 70°C due to the sensitivity of the measuring electrode at higher temperatures.

Table 4.61 Redox potential of various clearing agents under the conditions used for the clearing of the dyed samples

Compound	Redox potential (mV)
Sodium dithionite	-935
FAS/TUDO	-1000
Hydroxyacetone	-750
Glucose	-670
NS29076	+80
Laccase	+400
9,1-Anthraquinone-2-sulphonate (AQS)	-148
Sodium D-gluconate (DGL)	-137
Fe(II) sulphate + DGL	-624
Fe(III) chloride + DGL	-420

The redox potential values of all the compounds are broadly in line with previously reported values [217]. The results of the assessment of the clearing efficiency of these compounds are generally in accord with the measured redox potential values. FAS/TUDO has the highest negative redox potential among the reducing agents. Intuitively, FAS/TUDO as the most powerful reducing agent might thus be expected to be the most efficient clearing agent. Nevertheless, there are some exceptions, the most

notable of which is glucose. Most of the previous reports concerning the use of glucose as a reducing agent suggest that it has a lower negative redox potential and that a high temperature is required for the development of its full reduction potential. For example in a study, the redox potential of glucose was reported to be -610 mV at a temperature of 98°C [89]. However, some other studies report that glucose exhibited a maximum redox potential at about 60 - 70°C and no significant increase in redox potential was observed above 70°C [110, 111]. Glucose takes a longer time to reach its equilibrium redox potential as compared to sodium dithionite. It is reported that glucose takes about 30 minutes to reach a redox potential of about -600 mV vs Ag/AgCl while sodium dithionite reaches a potential of -600 mV in less than 5 minutes [98]. This was also noted during the measurement of redox potential in this study in terms of the time required to reach a stable reading.

Redox potential is a measure of the ability of a compound to accept or lose electrons which is always measured against a compound which acts as a reference. Measurement of redox potential is strongly influenced by the conditions of the system, the most important of which are pH and temperature. A compound may show various values of redox potential when measured under different conditions. Thus, all of these factors make the comparison of values measured at different times quite difficult and care should be taken in the comparison of values quoted from various studies.

Although in the study which forms the basis of this thesis, the measured redox potential of glucose is lower than the rest of the reducing agents, it was found to be as effective in improving the fastness properties of the dyed samples as compounds having a higher redox potential, such as sodium dithionite and FAS/TUDO. A similar case was observed with hydroxyacetone. Although its redox potential is significantly lower than sodium dithionite and FAS/TUDO, it performs equally well in the improvement of the fastness properties. It has been reported that despite having a lower redox potential than sodium dithionite and TUDO/FAS, hydroxyacetone is more stable towards atmospheric oxidation [11]. Hydroxyacetone degrades into a number of complex products in alkaline medium. The reducing action of hydroxyacetone is attributed, to a certain extent, to these products some of which have a higher negative redox potential than hydroxyacetone itself [209]. A similar degradation mechanism has been proposed for glucose, as discussed in depth in Section 2.6.3. Thus, a possible reason for the ability of glucose and hydroxyacetone to reduce compounds with higher negative redox potential may be the presence of these intermediate complex products.

In practice, there are other potential factors beside the redox potential that may influence the outcome, including the nature of the dye-fibre interactions and the extent of dye aggregation. The interaction of the reducing agent with the atmospheric oxygen is another possible contributing factor. For example, sodium borohydride has a higher negative redox potential than sodium dithionite but it has been found that it is unable to reduce vat dyes [45]. Nevertheless, the results throughout this investigation suggest that hydroxyacetone has potential in some cases as a reduction clearing agent for polyester, in spite of previous reports that higher temperatures than those used in this study are required for the agent to develop adequate reducing power.

The redox potential of laccase is +400 mV in the presence of HBT. This value is at the lower limit of the range of values reported previously (+400 mV to +800 mV). The redox potential of HBT is reported to be +1.085 mV [140]. Nevertheless, it has been reported that laccase can oxidise some compounds which have a higher redox potential than itself [139]. Although, NS29076 is a hydrolase and its potential ability to clear was not based on redox reactions, its redox potential was also measured. The value is quite low as was anticipated. Thus, laccase could not improve the washfastness properties by oxidation because its redox potential is not high enough and NS29076 did not exhibit any improvement because it has no significant redox properties.

It has been reported that the potentials exhibited by dye solutions are influenced significantly by the type of the solvent used as well as the pH of an aqueous medium. The mid-point potential ($E_{1/2}$) of water-soluble azo dyes is reported to be -0.6 to -0.7 V *vs* SCE in alkaline medium (pH 9.25) while in an acidic medium, the values increase to -0.2 to -0.3 V *vs* SCE. The anodic peak potential of most of the dyes studied lies in the range +700 mV to +1200 mV *vs* SHE [219]. Thus, in this study, it has been found that the redox potential values of the clearing agents are generally in accord with their ability to reduce or oxidise the dyes to provide the improvement that they have made in the fastness properties of the dyed samples.

4.10 Biochemical and Chemical Oxygen Demand

Samples of the residual liquor after the treatment of the samples dyed with dye **3** at 3% o.m.f. with the various clearing agents were sent to the laboratories of Scottish Water (Riccarton, Edinburgh) for the determination of chemical and biochemical oxygen demand of the clearing agents. It was ensured that the samples of residual liquor were

kept under the recommended conditions (0 - 4°C) and the test was carried out within 24 hours of collecting the liquors [220].

Biochemical oxygen demand is a measure of the oxygen uptake by microorganisms for the digestion of a compound in effluent. A high value of BOD indicates that there may be some oxygen depletion in the water stream when this effluent is discharged. Low levels of dissolved oxygen in the water stream may encourage the growth of anaerobic microorganisms. Anaerobes do not require oxygen for their metabolism, but rather they utilise sulphates for this purpose. Thus, anaerobes may reduce sulphates resulting in the formation of hydrogen sulphide which causes bad odour. Naturally, organic compounds are a staple food for the microorganisms and their BOD is higher than inorganic compounds. FAS/TUDO is an organic compound but with a high content of nitrogen and sulphur. Thus a low value of BOD does not necessarily indicate an environmentally sound compound. Compounds which are not digested by microorganisms also exhibit a low BOD value. Nevertheless, BOD is a useful parameter for assessing one aspect of the impact of the residual effluent on water streams. Chemical oxygen demand is the amount of oxygen consumed by a strong chemical oxidizing agent to oxidise compounds in the effluent. COD is higher than BOD as it contains the total oxygen demand of the effluent while BOD measures the amount of oxygen consumed in five days only. The COD value depends upon the oxidation state of carbon in the compound and aromatic hydrocarbons are only partially oxidized thus giving low values of COD [221]. For most industrial effluent, such as that released by the textile industry, the COD value is about 3 - 4 times the BOD value. The ratio of BOD/COD gives an indication of the biodegradability of the sample. A high ratio signifies that the sample is relatively biodegradable while a low ratio implies that the sample contains material which is not biodegradable or that the rate of biodegradation is very slow. The values of BOD and COD of the clearing agents used in this study are given in Table 4.62. Among the compounds tested, sodium D-gluconate (DGL) has the highest ratio of BOD/COD. It is known that DGL, glucose and hydroxyacetone are biodegradable and this explains the high values of BOD of these compounds.

As enzymes are proteins, their presence in the effluent might be expected to increase the BOD. However, the BOD of the residual liquor after clearing with the two enzymes, laccase and NS29076 used in this study is quite low as shown in Table 4.62. This may be due to the low concentrations of enzymes used in this treatment.

Table 4.62 Biochemical and chemical oxygen demand of various clearing agents after the treatment of dyed samples

Sample	BOD (mg l^{-1})	COD (mg l^{-1})	BOD/COD
Sodium dithionite	564	1710	0.33
TUDO/FAS	495	1780	0.28
Hydroxyacetone	1239	3215	0.39
Glucose	1723	4130	0.42
Sodium D-gluconate (DGL)	1117	1990	0.56
9,10-Anthraquinone-2-sulphonate (AQS)	<50	516	<0.096
Fe(III) sulphate + DGL	1427	3870	0.37
Detergent wash-off	127	911	0.14
Laccase	<30	330	<0.09
NS29076	353	735	0.48

Water quality is assessed by various chemical, physical and biological parameters which must be considered in relation to each other. In a five day period, biological oxidation is not complete and a five day BOD is about 80% of the ultimate BOD [222]. For example, in a study $(BOD)_5$ of reduction clearing effluent was reported to be 650 mg l^{-1} while degradation was only 24%. The $(BOD)_{28}$ of the same effluent was reported to be 1500 mg l^{-1} while degradation was only 55% [10]. Thus, ultimate biodegradation is another important parameter besides $(BOD)_5$ in the assessment of the water quality. It must be noted that BOD and COD do not take into account the products formed as a result of degradation. For example, the sulphates formed on the degradation of sodium dithionite may increase the conductivity of the water. The sulphates may also damage concrete structures by the formation of an alumino-sulphato complex which swells and cracks the concrete.

The COD value of the reduction clearing liquors with sodium dithionite and FAS/TUDO obtained in this study are quite low as compared to the values reported in previous studies [18, 223]. However, both sodium dithionite and FAS/TUDO increase the sulphur content of the effluent.

Chapter 5 - Conclusions

The objectives of this research described in this thesis were to establish a more definitive understanding of the principles of the traditional reduction clearing process and its effect on the properties of polyester dyed with a range of disperse dyes at different concentrations and, further, to explore a range of alternative clearing agents and processes which offer the potential to minimise the environmental consequences associated with the use of sodium dithionite. In spite of its commercial importance, there is remarkably little documented research aiming to quantify the outcome and the merits of reduction clearing in the dyeing of polyester. In this study, polyester fabric was dyed with a series of disperse dyes using a range of depths of shade and then subjected to a conventional reduction clearing process. The dyed samples were then evaluated in terms of the level of surface dye, and the colour and technical performance, both before and after reduction clearing. This investigation based on a series of selected disperse dyes, three from the azo chemical class and two anthraquinones, has confirmed quantitatively the general industrial observation that reduction clearing of disperse dyed polyester using sodium dithionite under alkaline conditions removes residual surface dye and has a consequent positive influence on the fastness and colour properties of the dyed fabric. The enhancement in the fastness properties due to clearing was quantified and the influence on the colour of the dyed fabrics was assessed. Fastness to washing, rubbing and perspiration are universally enhanced by the treatment, with especially significant improvements at higher depths of shade. However, the efficiency of removal of surface dye and the degree of influence on the properties varies significantly with the particular dye. Some of the dyes, dye **3** and dye **4**, had only a marginal improvement in the fastness properties after reduction clearing with sodium dithionite. The differences in behaviour have been correlated to an extent with specific features of the molecular structures of the dyes. For example, dye **2**, an azo dye having two ester groups which are potentially capable of alkaline hydrolysis is efficiently removed, whereas a dye with a similar structure but with no ester group, dye **3**, is much less efficiently removed. Dye **4** and dye **5** both have anthraquinone structures but dye **4** had poor fastness properties which are only improved marginally after reduction clearing with sodium dithionite. The structure of dye **4** has four electron releasing groups which increase its resistance to reduction. All of the dyed samples showed a modest increase in chroma after reduction clearing, a positive feature in terms of desirable colour properties. However, other features showed inconsistent trends, which may indicate complex colour-influencing phenomena associated with the removal of surface dye, conceivably involving opposing

effects. These may also be due to the rather small numerical values involved. Some broad correlations with chemical class are noted, for example a higher concentration of surface dye removal and an increase in colour depth after reduction clearing, as assessed by integ values, for the fabrics dyed with azo dyes as compared with the anthraquinones. However, such correlations would require further testing using a wider range of dyes.

Besides investigating the influence of reduction clearing on the fastness properties and colour properties of the dyed samples, the degree of surface dye removal was quantitatively determined by measuring the absorbance of the acetone extract of the dyed samples. It was demonstrated that this test method correlated well with the fastness properties. Generally, the degree of surface dye removal increased with the increasing depth of shade which at first sight appears strange. The only exception to this trend is dye **4**, whose degree of surface dye removal decreased with increasing depths of shade. However, a possible explanation for the general trend was proposed as that there may be a certain proportion of surface dye which is occluded in such a way that it is not removed by reduction clearing but is removed by acetone extraction, and that the level of this occluded dye increases with the increasing depth of shade. Another possibility may be that as the depth of shade increases, a higher amount of dye particles is present on the fibre surface which only has a loose interaction with the fibre. In contrast, at lower depths of shade, a lower amount of dye particles is present on the fibre surface but they are comparatively strongly attached with the fibre. Thus at higher depths of shade, a higher percentage of the dye particles may be removed. The scanning electron micrographs of the fabrics dyed with dye **4** dye show aggregates of particles which were not observed on the samples dyed with the other four dyes. This indicates that this particular dye may have a higher tendency towards aggregation which may explain its lower percentage of removal at higher depths of shade. Hence, the acetone extraction method has been established as a fairly quick and reasonably quantitative measure of the efficiency of removal of surface dye from dyed polyester.

Three organic reducing agents, FAS/TUDO, hydroxyacetone and glucose, were explored as alternatives to sodium dithionite in the reduction clearing of dyed polyester. It has been demonstrated that the clearing of polyester dyed with the five selected disperse dyes at depths of shade in the range 1-5% with the two organic reducing agents, FAS/TUDO and hydroxyacetone is efficient in terms of surface dye removal to an extent that provides excellent fastness properties, when used under the same

treatment conditions as sodium dithionite. Reduction clearing with glucose also improved the fastness and colour properties to a comparable level to that of sodium dithionite, albeit requiring a higher temperature of 90°C.

In terms of degree of surface dye removal, sodium dithionite proved to be marginally more efficient than both FAS/TUDO and hydroxyacetone in the case of one azo dye (dye **1**). However, the organic reducing agents were much more efficient than sodium dithionite in the case of one of the red azo dyes (dye **3**) and the two anthraquinones. With four of the dyes, the two organic reducing agents, FAS/TUDO and hydroxyacetone gave comparable performance. However, in the case of one anthraquinone dye, which is likely to be resistant to reduction based on its molecular structure, FAS/TUDO as the more powerful reducing agent proved to be significantly more efficient. In view of the observation that, broadly, FAS/TUDO and hydroxyacetone were more efficient, their use at a lower concentration was investigated for one red azo dye (dye **3**). Reduced efficiency of surface dye removal was observed at the lower concentration in both cases although, surprisingly, this effect was less in the case of hydroxyacetone. This preliminary result would need to be tested and verified with a wider range of dyes over a wider range of conditions. Nevertheless, the results throughout this investigation suggest that hydroxyacetone has potential in some cases as a reduction clearing agent for polyester, in spite of previous reports that higher temperatures than have been employed in this study are required for the agent to develop adequate reducing power.

Glucose proved to be significantly better than sodium dithionite in the case of all the dyes although used at a higher temperature. The exception was one blue anthraquinone dye (dye **5**) when it only gave comparable efficiency to that of sodium dithionite and a slight staining of nylon after the washfastness tests. A possible explanation for this staining is proposed as that the degradation products of dye after reduction with glucose have a tendency to stain nylon. This proposition is supported by the large shift in absorption maximum of the acetone extract of dyed samples after reduction clearing with glucose which changed from 666 nm for untreated to 623 nm for glucose. Although, a large shift in the absorption maxima is also observed in the case of dye **3**, the degradation products may not stain nylon so significantly. The dyed samples, with only a few exceptions, showed a moderate increase in chroma after reduction clearing with the four reducing agents, a positive feature in terms of desirable colour properties. Glucose again performed markedly superior to sodium dithionite in improving the

colour properties. The effect on colour of the removal of other surface impurities, such as oligomer, which was outside the scope of the present study, is also unpredictable. However, there is remarkable consistency in the trends in colour values produced by all the reducing agents.

The better performance of glucose in the removal of surface dye is confirmed by the scanning electron micrographs of the treated samples. Micrographs of samples dyed with dye **3** which appeared to respond only marginally to reduction clearing with sodium dithionite, showed appreciably cleaner fibre surface after reduction clearing with glucose. The redox potential of the reducing agents measured under these conditions of reduction clearing gave values of -935 mV for sodium dithionite, -1000 mV for FAS/TUDO, -750 mV for hydroxyacetone and -670 mV for glucose, broadly in line with previously reported values. Intuitively, FAS/TUDO as the most powerful reducing agent, might thus be expected to be the most efficient clearing agent with glucose least efficient. However, the results obtained from this study have showed that, despite having a comparatively lower redox potential, both hydroxyacetone and glucose perform equally well and in some cases better than sodium dithionite. This indicates that in practice, there are other potential factors besides redox potential that may influence the outcome, including the nature of the dye-fibre interactions and the extent of dye aggregation. A probable explanation for such unusual behavior of hydroxyacetone and glucose may lie in their reduction mechanisms. Both of these compounds undergo complex oxidation under alkaline medium resulting in the formation of a number of intermediate compounds most of which have enediol structures. Some of these intermediate compounds may have higher redox potential than the parent compound and thus providing a potential explanation for their ability to reduce compounds with much higher redox potential.

A similar study using a previously-reported detergent wash procedure demonstrated rather variable behaviour. In the case of the yellow azo dye (dye **1**), this process proved to be more efficient than reduction clearing especially at lower depths of shade. However, with the other dyes it was generally significantly less efficient. In contrast to the reduction clearing processes which involve chemical degradation of the surface dye and removal of the degradation products, the mechanism of the detergent wash presumably involves removal of dye molecules or aggregates as a result of the surface activity of the detergent species, with no chemical change. It is therefore likely that the ease of removal will be influenced by physical factors such as the degree of aggregation

of the dye and its interaction with the fibre surface. Indeed, the process was highly inefficient at removing the anthraquinone dye (dye **4**) which behaved differently from the other dyes in terms of the relationship between the efficiency of dye removal and depth of shade, a feature which was proposed as due to its tendency towards aggregation.

A parallel investigation based on similar methodology as that of reducing agents was carried out with enzymes as alternatives for the clearing of dyed polyester. Two different types of enzymes, one a hydrolase, NS29076 and the other an oxidoreductase, a laccase from *Trametes versicolor*, were studied in this regard. Treatment with NS29076 failed to improve the fastness or colour properties. This was probably due to the fact that its application might hydrolyse the polyester at its surface but with little anticipated effect on the dyes. In the case of the three azo dyes, a slight deterioration in the fastness properties was observed. There was no change in fastness properties of one of the anthraquinone dyes (dye **4**) while the washfastness properties of other blue anthraquinone dye (dye **5**) became markedly worse after treatment with NS29076. This result is interesting as it shows that NS29076 has probably interacted with the dyes in some way resulting in the formation of some degradation products which tend to stain multifibre fabric. Another possibility for the deterioration in washfastness properties has been suggested as that the treatment with NS29076 hydrolyse the surface of polyester but the hydrolysed superficial layer of polyester only comes off during the washfastness test because of the mechanical agitation resulting in the staining of adjacent multifibre fabric. Scanning electron micrographs of the treated samples also did not show any significant differences compared with the untreated samples. The degree of surface dye removal after the treatment was lower than after reduction clearing for three of the five dyes, two of which were azo dyes and one was an anthraquinone dye. The only two dyes for which NS29076 provided a comparable degree of surface dye removal were dyes **3** and **4**, both of which had responded poorly to reduction clearing with sodium dithionite.

Treatment with laccase also failed to improve the fastness properties of the three azo dyes. However, the fastness properties of one of the anthraquinone dyes (dye **4**) were improved to a comparable level to that of sodium dithionite. In contrast to NS29076, treatment with laccase did not cause any deterioration of the fastness properties. The measured redox potential of laccase in the presence of HBT was +400 mV which is less than the oxidation potential of a disperse dye which is generally around +700 mV to

+1200 mV. It is thus probable that laccase could not provide the required level of oxidation to provide a clearing effect. Thus, in this study, the two enzymes did not prove to be suitable alternatives to sodium dithionite for the clearing of dyed polyester. However, the results show that there is potential for further work in this area.

Another section of this study involved the investigation of electrochemical methods for potential application in the reduction clearing of dyed polyester. Only the CV of iron-TEA complex out of the three selected redox mediators showed an increase in current indicating that the dye is reduced. The other two mediators, iron-gluconate complex and AQS, could not reduce the dye as indicated by their respective CVs in the presence of dye **3**. The electrochemical reduction clearing experiments carried out at various values of potential and current failed to improve the fastness properties of the dyed polyester. This set of experiments was carried out to provide preliminary trials, the results of which showed promise. Further research is required to establish definitive conclusions.

As indicators of the environmental consequence of the processes in terms of effluent production, the chemical and biochemical oxygen demand values for the residual liquors were established. The residual liquors from clearing of samples dyed with dye **3** (3% o.m.f.) with FAS/TUDO gave slightly lower BOD and slightly higher COD than sodium dithionite. Hydroxyacetone and glucose gave substantially higher values, although they both offer the environmental advantage of biodegradability. The detergent wash process has been shown to enable a reduction in the BOD and COD compared with reduction clearing and also offers the potential to avoid generation of aromatic amines from the degradation of azo dyes. Although enzymes offer the advantage of lower environmental impact and they avoid the issue of the toxicity due to aromatic amines which are probably not formed, their application needs further investigation to improve their efficiency.

It can thus be concluded that organic reducing agents perform better than sodium dithionite as far as the improvement of the fastness and colour properties is concerned. However, for commercial acceptance, their cost and environmental effects have to be weighed. FAS/TUDO has almost similar influence on the effluent as sodium dithionite. It increases the sulphur and nitrogen content of the effluent. Hydroxyacetone and glucose have much higher BOD and COD values. However, both glucose and hydroxyacetone are biodegradable and are degraded into harmless compounds, water

and carbon dioxide. They also offer the advantage of sulphite and sulphate free effluent. The effluent from reduction clearing with glucose and hydroxyacetone can be treated to reduce the BOD and COD values. When all the reducing agents are compared on the basis of their current cost, glucose offers the most economical alternative as well as better clearing efficiency.

Chapter 6 - Future Work

Recommendations for possible future work are summarized below.

- The results of this research have shown that the use of enzymes, particularly the oxidases, for the reduction clearing of dyed polyester, has some potential. Further work to improve the efficiency of the enzymes for the dye removal may be carried out by employing various strategies. These may include:
    - The use of surfactants with enzymes.
    - A selection of various chemical compounds may be used as mediators with laccase to improve its action.
    - Laccase may also be used in a combination with other enzymes, for example with esterase or with other oxidases.
- An understanding of the reaction mechanism is necessary for improving the environmental sustainability of the reduction clearing process. The identification of the degradation products from the reduction of dye with glucose, hydroxyacetone and enzyme would be useful in understanding the mechanism of reduction. The degradation products of the dye can be isolated with preparative chromatography and characterized by FTIR, NMR or mass spectrometry.
- Reduction clearing with glucose may be further optimized for environmental effects using some activators.
- There is a need to improve the efficiency of electrochemical reduction clearing process. Future work can be carried out by the modification of the electrochemical cell to improve the flow of reducing species between the electrode and the fabric.
- This research has shown that some of the dyes respond better to degradation by oxidation. Thus, further explorations of the alternative methods for clearing may be made using oxidative methods such as ozone or peroxide.

Plasma can be explored as another alternative for clearing of dyed polyester fabric.

APPENDIX

Table 1 Colour measurements of samples dyed with dye **1** after reduction clearing with FAS/TUDO and hydroxyacetone

Shade (%)	Reducing agent	L*	a*	b*	C*	h°	Integ Value
1	Untreated	83.32	9	104.7	105.08	85.09	22.39
	FAS/TUDO	83.39	8.88	103.6	104.02	85.1	21.23
	Hydroxyacetone	83.12	8.94	103.3	103.68	85.05	21.3
2	Untreated	80.76	14.36	104.6	105.62	82.19	26.82
	FAS/TUDO	80.67	15.06	104.5	105.58	81.8	27.02
	Hydroxyacetone	80.71	15.17	104.9	105.98	81.77	27.56
3	Untreated	78.62	17.67	102.3	103.83	80.2	27.83
	FAS/TUDO	79.44	18.12	104.6	106.18	80.17	29.37
	Hydroxyacetone	79.67	18.41	105.1	106.68	80.06	29.5
4	Untreated	77.14	19.37	100.4	102.21	79.07	28.22
	FAS/TUDO	79.07	19.31	104.3	106.03	79.51	29.63
	Hydroxyacetone	79.09	19.28	104.5	106.23	79.54	29.99
5	Untreated	77.05	20.02	100.4	102.41	78.73	28.48
	FAS/TUDO	78.35	19.49	102.6	104.45	79.25	28.87
	Hydroxyacetone	78.44	19.54	103.1	104.89	79.27	29.43

Table 2 Colour measurements of samples dyed with dye **2** after reduction clearing with FAS/TUDO and hydroxyacetone

Shade (%)	Reducing agent	L*	a*	b*	C*	h°	Integ Value
1	Untreated	31.81	43.59	3.67	43.75	4.82	27.99
	FAS/TUDO	31.75	44.98	4.25	45.18	5.39	29.27
	Hydroxyacetone	31.8	44.97	4.28	45.17	5.44	29.15
2	Untreated	26.95	38.61	6.36	39.13	9.35	41.02
	FAS/TUDO	27.82	40.8	6.21	41.27	8.65	39.46
	Hydroxyacetone	27.77	40.95	6.26	41.42	8.69	39.84
3	Untreated	24.59	34.05	7.14	34.79	11.84	47.58
	FAS/TUDO	23.68	33.99	7.28	34.76	12.09	52.08
	Hydroxyacetone	23.84	33.96	7.21	34.71	11.98	51.16
4	Untreated	23.32	30.71	7.33	31.57	13.42	51.07
	FAS/TUDO	23.0	31.63	7.03	32.4	12.54	53.03
	Hydroxyacetone	22.91	31.79	7.14	32.58	12.67	53.81
5	Untreated	22.46	27.45	7.11	28.35	14.52	52.66
	FAS/TUDO	22.37	30.01	6.64	30.73	12.48	54.51
	Hydroxyacetone	22.38	30.19	6.72	30.93	12.55	54.7

Table 3 Colour measurements of samples dyed with dye **3** after reduction clearing with FAS/TUDO and hydroxyacetone

Shade (%)	Reducing agent	L*	a*	b*	C*	h°	Integ Value
1	Untreated	30.39	44.5	7.06	45.06	9.02	34.29
	FAS/TUDO	30.94	45.33	7.46	45.94	9.34	33.52
	Hydroxyacetone	30.88	45.02	6.97	45.55	8.8	33.1
2	Untreated	25.71	37.05	8.6	38.03	13.08	46.48
	FAS/TUDO	25.74	38.1	8.44	39.02	12.49	47.11
	Hydroxyacetone	25.8	37.98	8.79	38.98	13.03	47.06
3	Untreated	23.46	31.82	8.23	32.87	14.5	52.23
	FAS/TUDO	23.48	32.85	7.94	33.8	13.58	52.58
	Hydroxyacetone	23.05	32.81	8.01	33.77	13.72	54.92
4	Untreated	22.3	28.25	7.67	29.27	15.2	54.77
	FAS/TUDO	22.47	30.81	7.64	31.74	13.94	55.8
	Hydroxyacetone	22.17	30.67	7.76	31.63	14.2	57.5
5	Untreated	21.33	24.53	7.18	25.56	16.32	56.76
	FAS/TUDO	20.49	25.64	6.08	26.35	13.33	60.93
	Hydroxyacetone	20.74	25.31	6.01	26.01	13.36	59.06

Table 4 Colour measurements of samples dyed with dye **4** after reduction clearing with FAS/TUDO and hydroxyacetone

Shade (%)	Reducing agent	L*	a*	b*	C*	h°	Integ Value
1	Untreated	33.68	-0.37	-36.72	36.72	269.43	19.69
	FAS/TUDO	33.6	0.14	-37.36	37.36	270.21	19.95
	Hydroxyacetone	33.97	-0.08	-37.56	37.56	269.88	19.55
2	Untreated	25.01	4.93	-33.05	33.42	278.49	33.33
	FAS/TUDO	25.06	5.05	-34.15	34.52	278.41	34.39
	Hydroxyacetone	25.07	4.98	-33.66	34.03	278.42	33.77
3	Untreated	21.48	6.73	-29.26	30.02	282.96	40.17
	FAS/TUDO	21.61	6.63	-29.99	30.72	282.47	40.57
	Hydroxyacetone	21.64	6.71	-30.02	30.76	282.6	40.4
4	Untreated	20.21	7.02	-26.98	27.87	284.58	42.88
	FAS/TUDO	20.1	7.08	-27.71	28.6	284.33	44.02
	Hydroxyacetone	20.27	6.99	-27.49	28.37	284.26	43.15
5	Untreated	19.29	7.06	-25.28	26.25	285.61	45.33
	FAS/TUDO	19.41	6.93	-26.09	27	284.88	45.65
	Hydroxyacetone	19.26	7.03	-25.81	26.75	285.23	45.96

Table 5 Colour measurements of samples dyed with dye **5** after reduction clearing with FAS/TUDO and hydroxyacetone

Shade (%)	Reducing agent	L*	a*	b*	C*	h°	Integ Value
1	Untreated	54.25	-19.44	-30.52	36.19	237.5	6.01
	FAS/TUDO	54.97	-19.04	-33.15	38.23	240.14	5.92
	Hydroxyacetone	54.81	-18.96	-33.27	38.29	240.32	6
2	Untreated	45.37	-16.1	-33.06	36.77	244.04	11.6
	FAS/TUDO	46.81	-16.32	-34.6	38.26	244.75	10.8
	Hydroxyacetone	46.99	-16.49	-34.49	38.23	244.44	10.68
3	Untreated	40.82	-13.57	-33.99	36.6	248.24	15.8
	FAS/TUDO	41.97	-13.52	-35.24	37.74	249.01	14.83
	Hydroxyacetone	41.75	-13.50	-35.01	37.52	248.91	15.01
4	Untreated	37.2	-10.72	-34.05	35.69	252.52	19.3
	FAS/TUDO	37.7	-10.24	-35.42	36.87	253.87	19
	Hydroxyacetone	37.43	-10.08	-35.13	36.55	253.99	19.14
5	Untreated	34.16	-7.89	-34.12	35.02	256.98	22.65
	FAS/TUDO	34.38	-7.37	-35.13	35.9	258.16	22.59
	Hydroxyacetone	34.14	-7.21	-34.83	35.57	258.3	22.68

Table 6 Colour measurements of samples dyed with dye **1** after washing off treatment

Shade (%)		L*	a*	b*	C*	h°	Integ value
1	Untreated	82.78	8.67	103.07	103.43	85.19	21.53
	Washed-off	83.43	8.41	102.94	103.29	85.33	20.2
2	Untreated	79.87	13.99	102.58	103.53	82.24	25.9
	Washed-off	81.11	13.85	103.88	104.8	82.4	24.88
3	Untreated	79.01	15.66	101.9	103.1	81.26	26.69
	Washed-off	79.98	15.91	102.97	104.19	81.22	25.9
4	Untreated	77.98	18.45	101.28	102.94	79.68	27.53
	Washed-off	79.52	18.26	103.28	104.88	79.97	26.79
5	Untreated	74.98	20.37	96.29	98.42	78.06	27.69
	Washed-off	75.8	20.68	96.99	99.17	77.96	26.74

Table 7 Colour measurements of samples dyed with dye **2** after washing off treatment

Shade (%)		L*	a*	b*	C*	h°	Integ value
1	Untreated	32.05	44.39	4.2	44.59	5.41	28.17
	Washed-off	32.4	44.93	3.43	45.06	4.36	27.22
2	Untreated	26.96	38.55	6.62	39.12	9.75	41.12
	Washed-off	27.11	39.37	6.03	39.82	8.71	40.79
3	Untreated	24.56	34.34	7.39	35.13	12.15	48.3
	Washed-off	24.68	35.33	6.85	35.99	10.97	48.07
4	Untreated	23.04	30.51	7.48	31.41	13.78	52.48
	Washed-off	22.99	31.28	6.64	31.98	11.99	52.4
5	Untreated	22.22	27.37	7.25	28.31	14.84	54.02
	Washed-off	22.05	28.65	6.44	29.37	12.66	54.89

Table 8 Colour measurements of samples dyed with dye **3** after washing off treatment

Shade (%)		L*	a*	b*	C*	h°	Integ Value
1	Untreated	30.21	44.48	7.26	45.07	9.27	35.02
	Washed-off	29.98	45.17	7.86	45.85	9.87	36.93
2	Untreated	25.59	38.64	9.3	39.74	13.54	49.51
	Washed-off	25.41	39.19	9.31	40.28	13.36	50.99
3	Untreated	23.11	33.35	8.87	34.51	14.9	56.39
	Washed-off	22.96	33.7	8.73	34.81	14.52	57.39
4	Untreated	21.49	29.1	8.33	30.26	15.98	61.06
	Washed-off	21.67	30.33	8.22	31.43	15.16	60.98
5	Untreated	20.69	25.72	7.54	26.8	16.33	61.96
	Washed-off	20.73	26.93	7.36	27.92	15.29	62.44

Table 9 Colour measurements of samples dyed with dye **4** after washing-off treatment

Shade (%)		L*	a*	b*	C*	h°	Integ Value
1	Untreated	33.31	-0.79	-36.15	36.16	268.74	20.26
	Washed-off	32.68	0.12	-36.98	36.98	270.19	21.46
2	Untreated	25.41	4.14	-33.38	33.64	277.07	33.23
	Washed-off	25.57	4.45	-34.38	34.67	277.37	33.58
3	Untreated	22.42	5.83	-31.05	31.6	280.63	39.49
	Washed-off	22.39	6.26	-31.67	32.28	281.18	39.86
4	Untreated	19.95	6.94	-27.8	28.66	284.01	44.9
	Washed-off	20.07	7.19	-28.3	29.19	284.26	44.64
5	Untreated	19.27	6.85	-25.06	25.98	285.3	45.38
	Washed-off	18.81	7.31	-25.89	26.91	285.77	47.84

Table 10 Colour measurements of samples dyed with dye **5** after washing-off treatment

Shade		L*	a*	b*	C*	h°	Integ value
1%	Original	55.09	-20.1	-30.71	36.71	236.79	5.75
	Washed-off	56.11	-18.65	-33.25	38.12	240.71	5.37
2%	Original	46.4	-17.15	-33.26	37.43	242.72	11.05
	Washed-off	47.79	-16.53	-34.82	38.55	244.61	10.11
3%	Original	42.86	-15.41	-33.58	36.95	245.35	14.01
	Washed-off	44	-14.87	-34.55	37.62	246.72	12.89
4%	Original	37.54	-11.55	-33.86	35.77	251.17	19.17
	Washed-off	38.35	-10.97	-34.61	36.3	252.42	17.93
5%	Original	34.59	-9.04	-33.63	34.82	254.95	22.33
	Washed-off	35.1	-8.52	-34.34	35.38	256.07	21.55

Table 11 Absorbance values of the acetone extracts of the samples dyed with dye **3** (3% o.m.f.) after treatment with NS29076 for optimisation

Conc. of NS 29076 (ml l^{-1})		Temp.	Time	Absorbance					
	pH	°C	hr	Control 1	Sample 1	Control 2	Sample 2	Control 3	Sample 3
1	8	40	2	1.25	1.00	1.41	0.82	1.20	0.84
1	8	40	4	1.11	1.02	1.08	0.88	1.21	0.82
1	8	40	1	1.27	1.27	1.28	1.08	1.11	0.99
1	8	40	0.5	1.50	1.20	1.53	1.31	1.45	1.42
2	8	40	2	1.27	0.97	1.30	0.83	1.33	1.00
5	5	60	2	1.27	0.86	1.36	0.84	1.16	0.87
10	5	60	2	1.32	0.86	1.42	0.67	1.23	0.80
1	8	50	2	1.43	1.39	1.37	1.12	1.42	1.29
1	8	60	2	1.24	0.83	1.20	0.99	1.13	0.97
1	5	60	2	1.22	0.87	1.21	0.70	1.32	0.67
1	9	60	2	1.34	1.20	1.27	1.21	1.28	0.90
1	5	40	2	1.33	1.21	1.37	1.27	1.38	1.20
1	5	70	2	1.16	0.85	1.07	0.77	1.28	0.86

Table 12 Washfastness of the samples dyed with dye **3** (3% o.m.f.) after treatment with NS29076 at 60°C, pH 5 for 2 hrs at varying concentrations of enzyme

Concentration of NS29076 (ml l^{-1})	1	5	10
Washfastness-Staining			
Wool	3-4	3-4	3-4
Acrylic	4-5	4-5	4-5
Polyester	3	3-4	3-4
Nylon	2	1-2	1-2
Cotton	4-5	4-5	4-5
Acetate	2	2-3	2-3

Table 13 Washfastness of the samples dyed with dye **3** (3% o.m.f.) after treatment with NS29076 at pH 5 for 2 hours at 60°C and 70°C

Temperature	60°C	70°C
Washfastness-Staining		
Wool	3-4	3-4
Acrylic	4-5	4-5
Polyester	3	3-4
Nylon	2	2
Cotton	5	4-5
Acetate	2	3

Table 14 Absorbance values of the acetone extracts of the samples dyed with dye **3** (3% o.m.f.) after treatment with laccase for optimisation

Laccase	HBT	pH	Temp	Time	Control			Sample		
(10^3 U l^{-1})	(mM l^{-1})		(°C)	(hr)	1	2	3	1	2	3
1	1	5	30	48	1.23	1.43	-	0.67	0.79	-
1	1	5	30	40	1.49	1.41	-	0.78	0.58	-
1	1	5	30	28	1.26	1.40	-	0.78	0.77	-
1	0	5	30	24	1.83	1.79	-	1.63	1.75	-
1	1	5	30	24	1.83	1.79	-	1.14	0.78	-
1	1	5	30	20	1.47	1.35	-	0.79	0.69	-
1	1	5	30	18	1.44	1.29	-	0.70	0.71	-
1	1	5	30	14	1.40	1.53	-	0.77	0.71	-
1	1	5	30	8	1.47	1.48	1.46	0.75	0.85	0.83
1	1	5	30	7	1.26	1.40	1.32	0.70	0.73	0.69
1	1	5	30	4	1.30	1.33	1.32	0.90	0.79	0.94
1	1	5	30	2	1.46	1.38	1.46	0.91	0.80	0.83
1	1	5	30	1	1.38	1.28	1.18	0.95	0.98	1.00
1	0.5	5	30	2	1.42	1.37	1.49	1.22	1.18	1.18
1	2	5	30	2	1.34	1.48	1.36	0.98	0.96	0.98
1	5	5	30	2	1.34	1.48	1.36	1.03	0.82	0.86
1	1	5	25	2	1.49	1.48	1.41	1.10	1.07	1.08
1	1	5	40	2	1.24	1.33	1.18	0.67	0.67	0.77
1	1	5	50	2	1.35	1.30	1.34	0.75	0.71	0.71
1	1	3	40	2	1.52	1.49	1.31	1.31	1.21	1.22
1	1	7	40	2	1.45	1.24	1.34	1.47	1.42	1.41
0.5	1	5	40	2	1.47	1.39	1.40	0.83	0.92	0.95
1.5	1	5	40	2	1.40	1.31	1.43	0.63	0.72	0.68
2	1	5	40	2	1.38	1.43	1.45	0.76	0.80	0.77

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